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DETERMINATION OF THE PURITY OF HYDROCARBONS BY MEASUREMENT OF FREEZING POINTS[1]

By Augustus R. Glasgow, Jr., Anton J. Streiff,[2] and Frederick D. Rossini

ABSTRACT

An improved and simplified procedure is described for determining the freezing points of hydrocarbons from time-temperature freezing and melting curves, and for calculating the purity when the freezing point for zero impurity is (a) known and (b) not previously known. A procedure for determining the cryoscopic constant is also described.

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I. INTRODUCTION

In connection with the work of this laboratory on the analysis, purification, and properties of hydrocarbons, the freezing point, determined from time-temperature freezing and melting curves, has been used to evaluate the purity of given samples of hydrocarbons. Since the previous reports on this subject [1, 2, 3],* improvements have been made in the apparatus and the procedure has been clarified and simplified. This report describes the present apparatus and procedure for determining the freezing point from time-temperature freezing and melting curves and for calculating the purity when

[1] This investigation was performed at the National Bureau of Standards as part of the work of the American Petroleum Institute Research Project 6 on the "Analysis, Purification, and Properties of Hydrocarbons."

[2] Research Associate on the American Petroleum Institute Research Project 6 at the National Bureau of Standards.

* Figures in brackets indicate the literature references at the end of this paper.

the freezing point for zero impurity is known and also when the freezing point for zero impurity is not previously known. A procedure for determining the cryoscopic constant is also described.

II. PRINCIPLES INVOLVED

The definitions, abbreviations, and symbols used in this paper are the same as those given in the preceding report [2], to which the reader is referred for details not covered here.

For the equilibrium between a crystalline phase consisting of the major component alone and a liquid phase consisting of the major component and one or more other components, the thermodynamic relation between the temperature of equilibrium and the composition of the liquid phase, for an ideal or sufficiently dilute solution, is

$$-\ln N_1 = -\ln (1-N_2) = A(t_{f_0}-t)[1+B(t_{f_0}-t)+ \ . \ . \ .], \tag{1}$$

where

N_1 = the mole fraction of the major component in the liquid phase;

$N_2 = (1-N_1)$ = the sum of the mole fractions of all other components in the liquid phase;

t_{f_0} = the temperature, in degrees centigrade, of the freezing point of the major component when pure (that is, when $N_2=0$);

t = the given temperature of equilibrium, in degrees centigrade;

$A = \Delta H_{f_0}/RT_{f_0}^2$;

$B = 1/T_{f_0} - \Delta C_{p_0}/2\Delta H_{f_0}$;

R = the gas constant, per mole;

$T_{f_0} = t_{f_0} + 273.16$

ΔH_{f_0} = the heat of fusion; per mole, of the major component in the pure state at the temperature T_{f_0};

ΔC_{p_0} = the heat capacity, per mole, of the pure liquid less that of the pure solid, for the major component in the pure state at the temperature T_{f_0}.

It is seen that the three constants (t_{f_0}, A, and B) in eq 1 are properties only of the major component, so that the relation between the temperature of equilibrium and the mole fraction of solute is the same for all solutes, of which there may be more than one in the same solution, provided they remain in the liquid phase and form with the major component an ideal solution.

If r is the fraction crystallized of the total number of moles of all components in the system, then, as previously shown [2],

$$t = t_{f_0} - a/[\{1-(b/a)\}-r], \tag{2}$$

where a and b are constants for the given sample. Equation 2 gives

the relation between the temperature of equilibrium and the fraction of material crystallized.

When the experiment is one performed according to the procedure described in the present report, the rate of crystallization or melting of the major component is substantially constant with time, and, as previously shown [2],

$$r=k(z-z_f), \tag{3}$$

where k is a constant characteristic of the given experiment, z is any given time, and z_f is the time at which freezing begins or melting is complete. Furthermore,

$$t=t_{f_0}-a'/[1-k'(z-z_f)], \tag{4}$$

where a' and k' are constants [2]. Equation 4 gives the relation between the temperature of equilibrium and the time during the part of the experiment in which equilibrium between the liquid and solid phases of the major component exists.

III. APPARATUS AND MATERIALS

The freezing-point apparatus in its present form is shown in figures 1, 2, and 3, which give, respectively, the assembly, the details of the freezing tube,[3] and the details of the stirring assembly. With the stirrer shown in figure 3, the vertical stroke is usually made 1½ inches over-all, and the rate about 120 strokes per minute.

The thermometric system consists of a 25-ohm platinum resistance thermometer, a resistance bridge (Müeller-type)[4] in which the main coils are thermostated, and a highly sensitive galvanometer, adjusted so that 1 mm on the scale is equivalent to from 0.0001 to 0.0005 degree centigrade.

The apparatus also includes a vacuum system and a stop watch or clock.

The cooling and warming baths used are listed in table 1.

TABLE 1.—*Cooling and warming baths used*

Type of experiment	Range of freezing points	Cooling or warming bath
	°C	
Freezing	+30 to −50	Slush of solid carbon dioxide in a 50–50 mixture of carbon tetrachloride and chloroform.
Do	−50 to −170	Liquid air, or preferably, liquid nitrogen.
Melting	+30 to −10	Water maintained constant (±1 degree centigrade) at 10 to 25 degrees centigrade above the freezing point of the sample.
Do	−10 to −90	Ice and water.*
Do	−90 to −170	Slush or solid carbon dioxide in a 50–50 mixture of carbon tetrachloride and chloroform.*

* See the discussion at the end of section V.

[1] Acknowledgment is gratefully made of the assistance of F. W. Rose, Jr. (formerly Research Associate on the API Research Project 6, and since October 1940, with the Houdry Process Corporation, Marcus Hook, Pa.), in fixing the details of the first design of the freezing tube shown in figure 2.

[3] Leeds & Northrup No. 8069, type G–2.

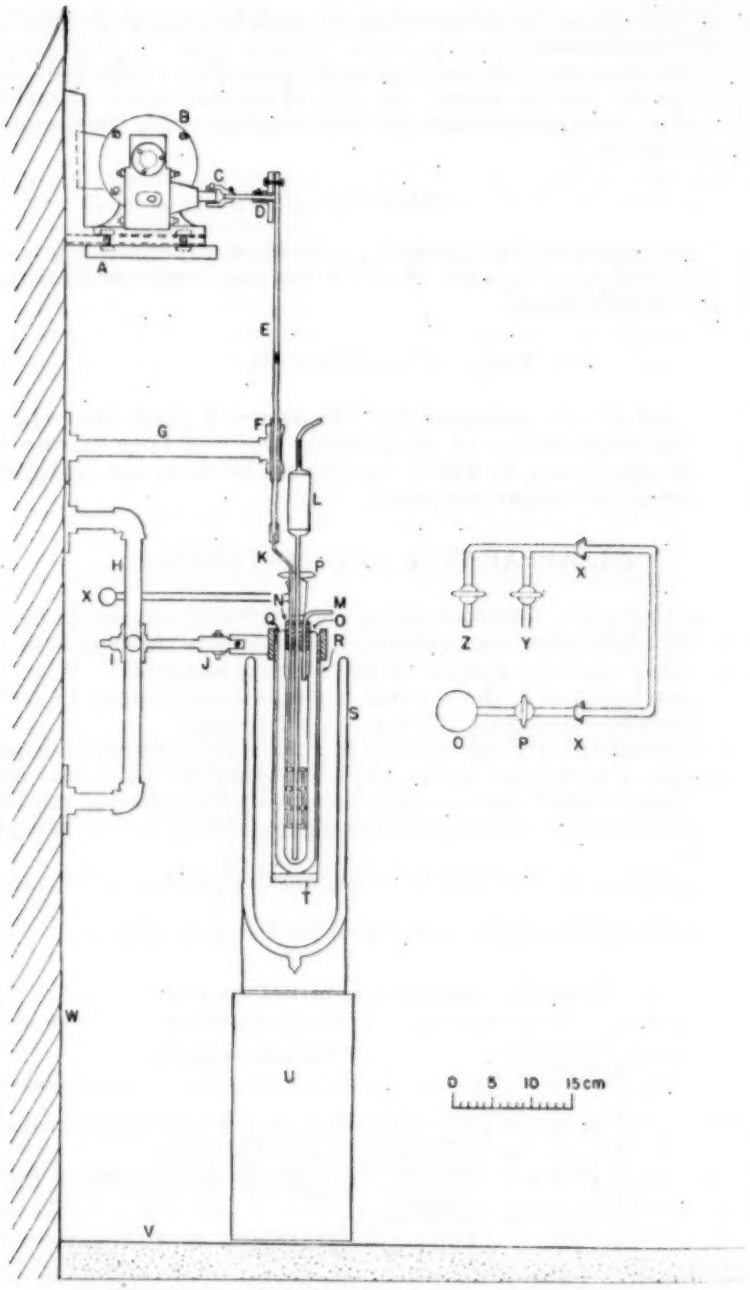

FIGURE 1.—*Assembly of the freezing-point apparatus.*

A, Bracket for motor, with rubber pad; *B*, motor, with reduction gears, to give 120 rpm; *C*, coupling; *D*, wheel; *E*, steel rod; *F*, bearing; *G*, support for bearing; *H*, support for freezing tube; *I*, adjustable clamp holder; *J*, clamp for freezing tube; *K*, stirrer; *L*, thermometer; *M*, tube for inlet of dry air; *N*, cork stopper, with holes as shown, plus a small hole for the "seed" wire; *O*, freezing tube, with silvered jacket; *P*, stopcock on freezing tube; *Q*, asbestos collar; *R*, brass cylinder, 12½ inches long and 2⅛ inches inside diameter, with Bakelite collar; *S*, Dewar flask, for cooling or warming bath; *T*, asbestos pad at bottom of cylinder *R*; *U*, wood-block support; *V*, table top; *W*, wall; *X*, spherical joint, 18/7; *Y*, connection to vacuum; *Z*, connection to air, through drying tube.

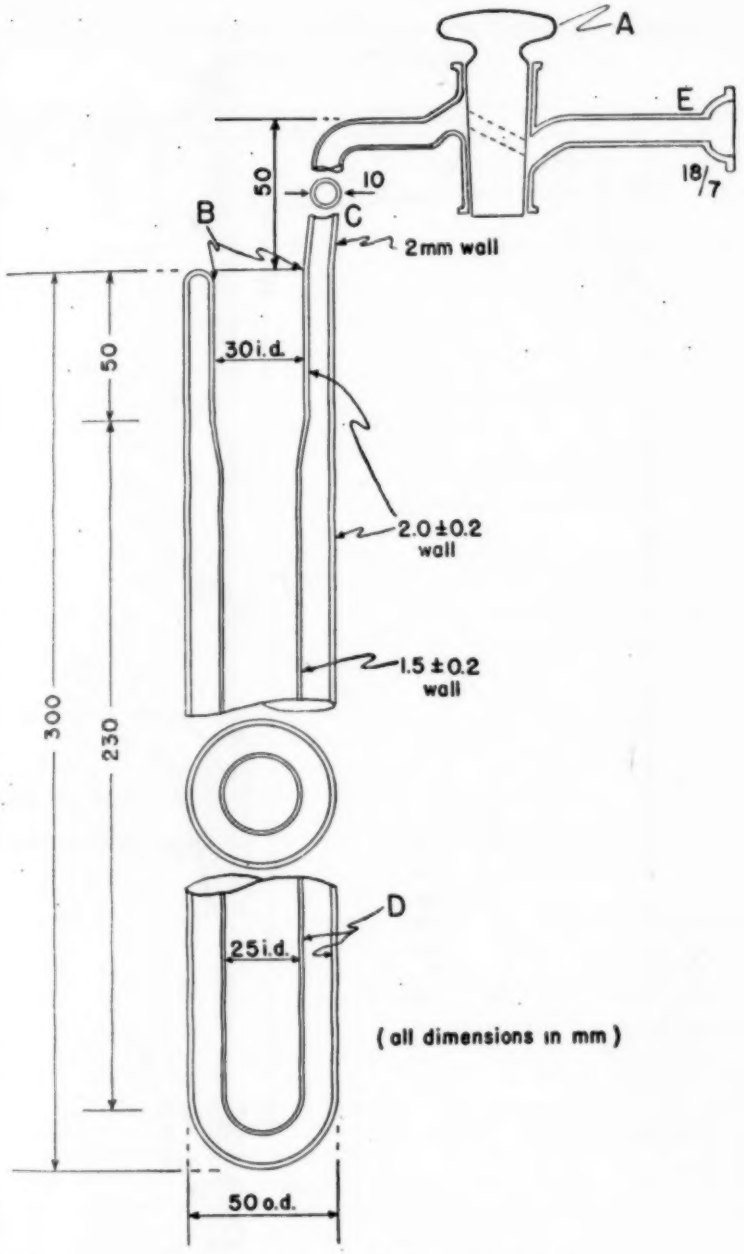

FIGURE 2.—*Details of the freezing tube.*

A, High-vacuum stopcock, hollow plug, oblique 3½-mm bore; *B*, inside opening of freezing tube, which must have no bulge at this point; *C*, slanted connection to jacket of freezing tube; *D*, internal walls of jacket of freezing tube, silvered; *E*, spherical joint, 18/7.

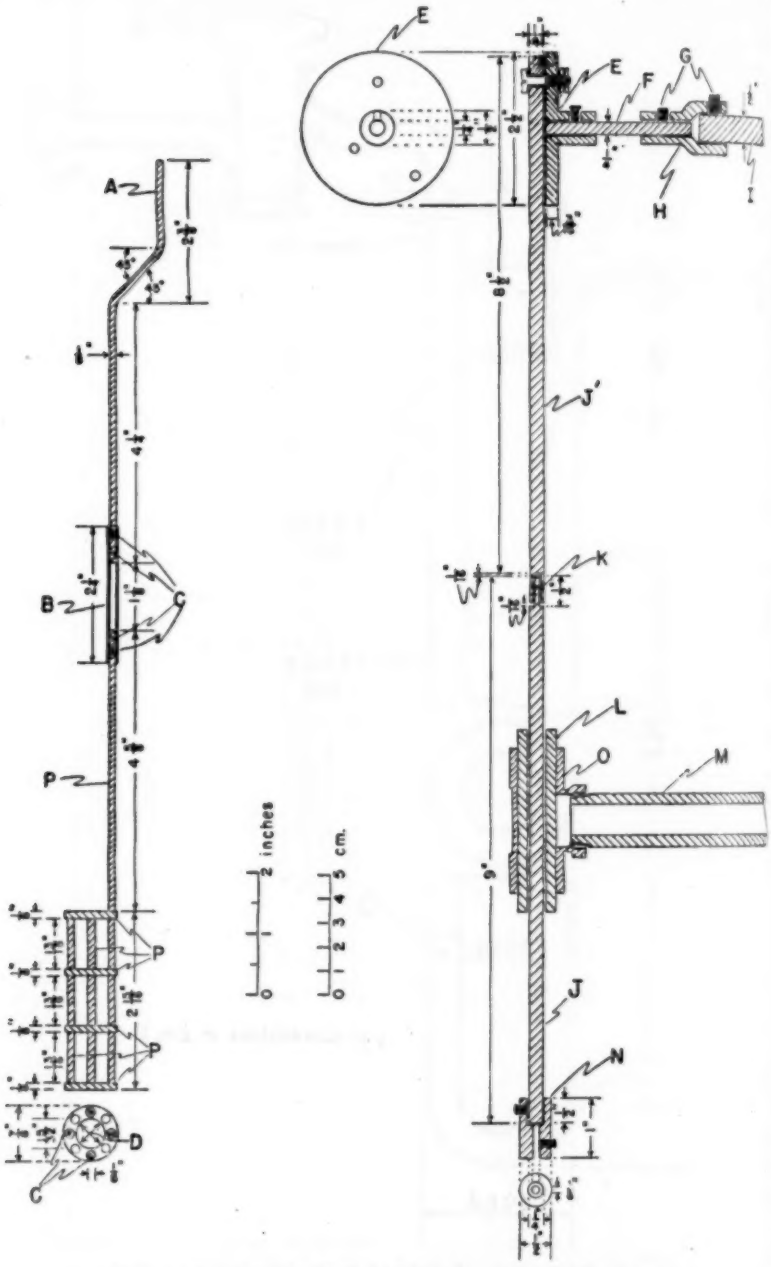

FIGURE 3.—*Details of the stirring assembly and supports.*

A, Stainless steel rod, round; *B*, German-silver tube; *C*, pins; *D*, holes, ¼-inch in diameter; *E*, brass wheel with three holes, tapped for machine screws, spaced ½, ¾, and 1 inch from center; *F*, steel rod; *G*, set screws; *H*, brass coupling; *I*, steel shaft; *J*, steel rod, round; *J'*, steel rod, square; *K*, connecting pin; *L*, brass-sleeve bearing; *M*, steel pipe, ¼-inch nominal size; *N*, brass coupling; *O*, brass tee; *P*, aluminum.

IV. EXPERIMENTAL PROCEDURE FOR A FREEZING EXPERIMENT

The procedure for performing a freezing experiment is as follows: The apparatus is assembled, with no refrigerant and no sample of hydrocarbon yet in place, but with a stream (10 to 20 ml a minute) of dry air flowing. The jacket of the freezing tube is filled with air freed of carbon dioxide and water.

As required, the operator must be prepared to induce crystallization in the hydrocarbon sample as soon as possible after the temperature has passed below the freezing point of the sample. In some cases, crystallization may be induced by introducing, into the hydrocarbon sample at the appropriate time, a small metal rod, which has been kept at liquid air temperatures. In other cases, crystallization may be induced by introducing, into the hydrocarbon sample at the appropriate time, crystals of the hydrocarbon on the coiled end of a small metal rod. These crystals are made by placing several milliliters of the hydrocarbon in a small test tube (incased in a thin metal tube) immersed in a refrigerant whose temperature is below the freezing point of the hydrocarbon.

The Dewar flask surrounding the freezing tube is filled with the appropriate refrigerant. The thermometer and stopper are temporarily removed and the hydrocarbon sample (50 ml of liquid) is introduced. When the hydrocarbon is volatile or normally gaseous at room temperature, the freezing tube is cooled before introducing the sample in order to minimize loss by evaporation. The flow of dry air into the freezing tube is continued in order to keep out water vapor. The stirrer is started and the sample is allowed to cool down to within about 15 degrees centigrade of the freezing point, when evacuation of the jacket of the freezing tube is begun.

The time and the resistance of the thermometer are observed at even intervals of 0.1 ohm (about 1 degree centigrade) to determine the rate of cooling. When a cooling rate is obtained that will give a change of 1 degree in about 2 to 3 minutes, in the range of about 5 to 10 degrees above the freezing point, the stopcock controlling the jacket of the freezing tube is closed. (The optimum rate of cooling will vary with the hydrocarbon being examined.)

When the temperature reaches a point about 5 degrees above the expected freezing point, the time is recorded to 1 second (or 0.01 minute), at which the resistance of the termometer equals certain preselected values (every 0.1 or 0.05 ohm). At the appropriate time (see above), crystallization is induced. The beginning of crystallization will be accompanied by a halt in the cooling of the liquid. After recovery from under cooling is substantially complete, the resistances, including the reading of the scale of the galvanometer at full sensitivity as well as the scale reading with no current through the galvanometer, are recorded at intervals of about 1 minute. These observations, together with the sensitivity of the galvanometer system in terms of ohms per millimeter of scale reading, yield a sensitivity near 0.0001 degree centigrade in the measurement of temperature. These observations are continued until the stirrer begins laboring.

Then the stirrer is stopped and comparison of "N" and "R" readings

is made through the commutator. These latter readings are made at fixed intervals of about 1 minute, alternately for "N" and "R," and the difference between the two at any given instant of time is determined from a plot of the several values against time.

V. EXPERIMENTAL PROCEDURE FOR A MELTING EXPERIMENT

The procedure for performing a melting experiment is exactly the same as for a freezing experiment, up to the point where the stirrer begins laboring. When the stirrer shows signs of laboring, a comparison of "N" and "R" readings is made through the commutator as in the previous section, except that the stirrer is still operating. When the laboring of the stirrer becomes quite pronounced, the cooling bath is replaced by the appropriate warming bath, and, simultaneously, further evacuation of the freezing tube is begun with the stirrer still operating. After evacuation for an appropriate length of time (3 to 10 minutes), the stopcock on the freezing tube is closed, and observations of time and resistance are continued along the equilibrium portion of the melting curve as along the equilibrium portion of the freezing curve. When melting is substantially complete, as evidenced by a marked change in the rate of change of resistance, the time is recorded when the resistance reaches certain preselected values at even intervals of 0.05 ohm (0.5 degree centigrade). The experiment is concluded when the temperature has reached a point 5 to 10 degrees above the freezing point.

For substances having freezing points in the range −135° to −170° C, the melting experiment may be performed by letting the cooling bath of liquid air remain in position and evacuating the jacket of the freezing tube as much as possible. This will make the thermal conductivity across the jacket so small that the energy introduced by the stirrer may be used to provide the energy of melting. A similar procedure may be used for melting experiments with substances having freezing points in the range from about −50 to −80° C, utilizing the bath of solid carbon dioxide in a 50-50 mixture of carbon tetrachloride and chloroform.

VI. EVALUATION OF THE FREEZING POINT FROM A FREEZING CURVE

To locate zero time (the time at which crystallization would have begun in the absence of undercooling), a preliminary plot is made of the time-resistance observations covering the liquid cooling line and the equilibrium portion of the freezing curve. For this plot, as shown in figure 4, the time scale is taken so that 1 cm is equivalent to 1 minute and the resistance scale (for a 25-ohm thermometer) so that 1 cm is equivalent to 0.02 ohm (0.2 degree centigrade). Usually the extent of undercooling is small enough that no correction for zero time need be made, in which case zero time can usually be determined by a visual extrapolation, on this plot, of the equilibrium portion of the freezing curve back to its intersection with the liquid-cooling line. However, if undercooling is appreciable, correction for its effect on the time may be required (see part II–2 of reference [1]).

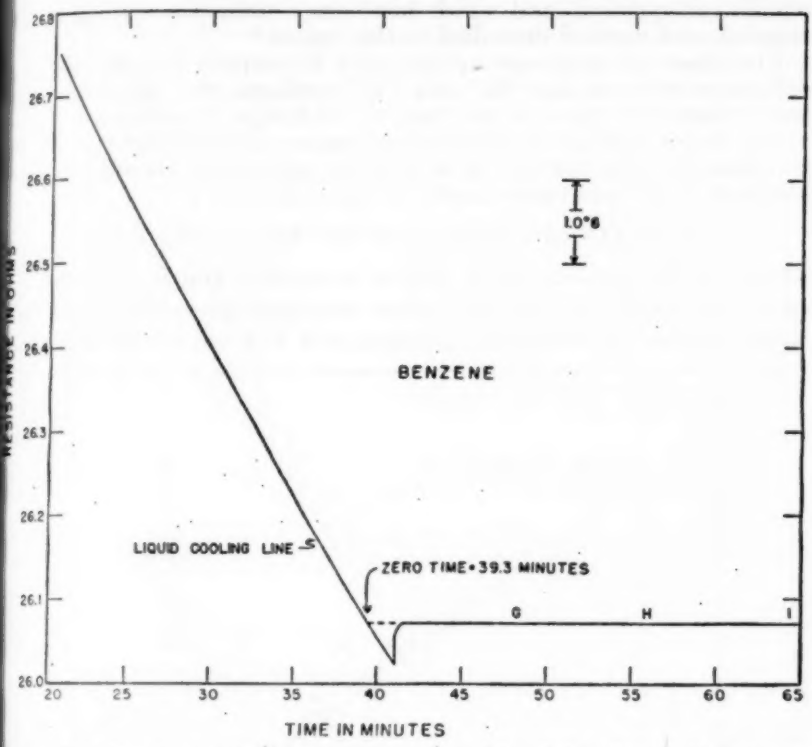

FIGURE 4.—*Time-temperature cooling curve for determining "zero" time in an experiment on a sample of benzene.*

The scale of ordinates gives the resistance in ohms of the platinum resistance thermometer, and the scale of abscissas gives the time in minutes. GHI represents the equilibrium portion of the freezing curve. Zero time is given by the intersection of the liquid cooling line with GHI extended. The same data are plotted in figure 5 with a magnified scale of temperature.

In order to locate accurately the resistance corresponding to the freezing point, the time-resistance observations are plotted as shown in figure 5, with the same time scale as before but with the scale of temperature magnified 10 to 200 times. The equilibrium portion of the curve, GHI, is extended back to its intersection at F with the liquid line by the simple geometrical construction shown in figure 6 (taken from reference [2]), selecting, for this purpose, three points (near the ends and the middle) of the equilibrium portion of the curve. The point F gives the resistance corresponding to the freezing point. (For details regarding the identification of the equilibrium portion of the curve, and the geometrical construction for determining the freezing point, see reference [2].)

If there is any doubt about the location of the equilibrium portion of the time-temperature curve, the criterion described on pages 210 and 211 of reference [2] may be applied. This procedure [2] involves plotting values of $(z-z_m)/(R-R_m)$ versus $(z-z_m)$, where (R_m, z_m) is an arbitrary fixed point near the middle of the equilibrium portion and (R, z) is any other point on the curve. This plot yields a straight line for that portion of the time-termperature curve representing the

equilibrium portion, and which has been obtained according to the experimental method described in this report.[5]

The observed resistance at the point F, corrected by one-half the difference between the "N" and "R" readings, and by appropriate calibration corrections to the coils of the bridge, if necessary, is converted to temperature in degrees centigrade. A convenient procedure to follow for this purpose is to put the calibration constants of the platinum resistance thermometer in the equation

$$R=R_0\{1+ct[(1+0.01\delta)-10^{-4}\delta t-10^{-8}\beta(t-100)t^2]\}, \quad (5)$$

where t is the temperature in degrees centigrade and R_0, δ, β, and c, $=(R_{100}-R_0)/100R_0$, are the calibration constants provided by the National Bureau of Standards Thermometer Laboratory for the given

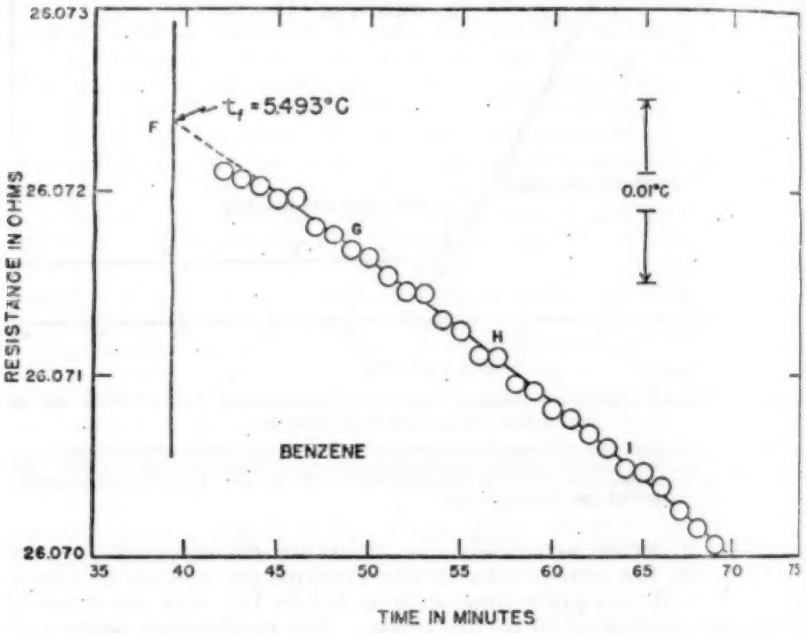

FIGURE 5.—*Time-temperature cooling curve for determining the freezing point of a sample of benzene.*

The scale of ordinates gives the resistance in ohms of the platinum resistance thermometer, and the scale of abscissas gives the time in minutes. GHI represents the equilibrium portion of the freezing curve. The freezing point F is determined as described in the text (see [2]). These data are the same as those plotted in figure 4.

thermometer. The foregoing equation with four constants is used for the range −190° to 0° C. For the range above 0° C, β is taken as zero, and the equation is simplified to

$$R=R_0\{1+ct[(1+0.01\delta)-10^{-4}\delta t]\}. \quad (6)$$

With this equation, values of R are calculated to 0.00001 ohm, for unit degrees in the range of interest. (If determinations are to be

[5] This plot of $(z-z_m)/(R-R_m)$ versus $(z-z_m)$ may also be used to evaluate t_f and t_{f_2}, as described on pages 210 and 211 of reference [2].

made on many different hydrocarbons, time will be saved by making up at the start a table of such values of R for unit degrees in the entire range). Linear interpolation between unit degrees may be used without significant error to obtain the temperature corresponding to the given resistance. A table of this kind covering the range −190° to 50° C can be put on a sheet 14 by 17½ inches in size.

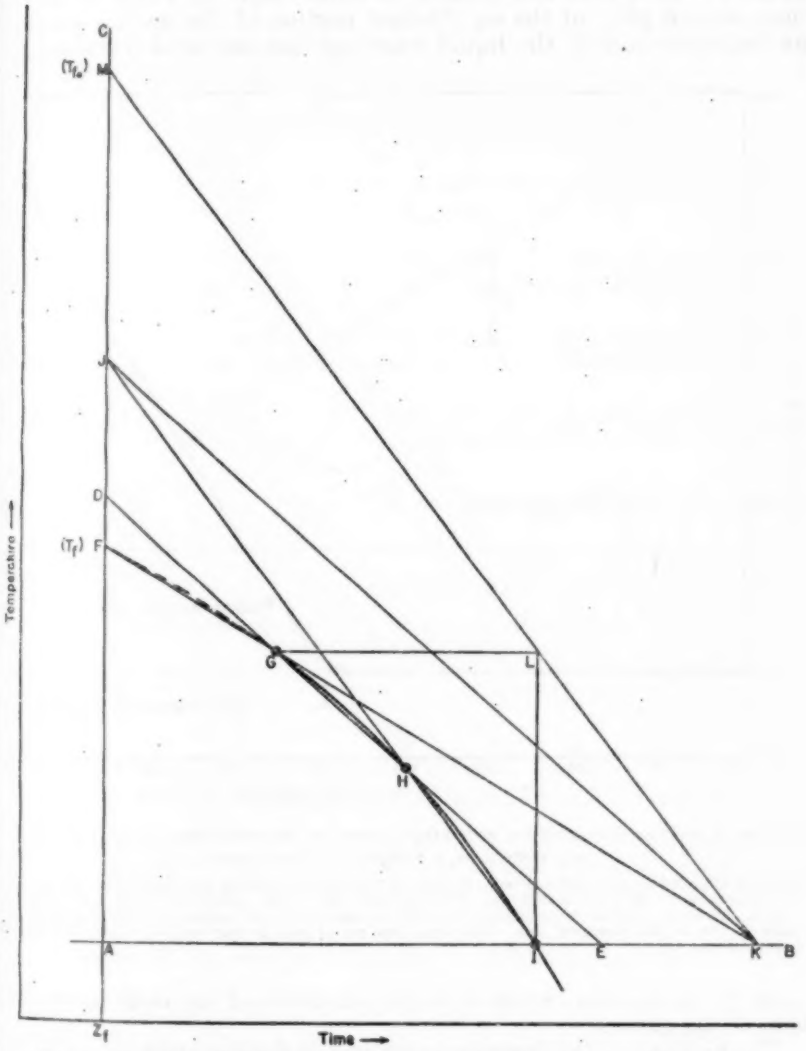

FIGURE 6.—*Geometrical construction for determining the freezing point.*

Given G, H, and I as any three points on the equilibrium portion of the freezing curve, preferably spaced approximately as shown. Construction to determine t_f: Draw AC parallel to the temperature axis at "zero" time (the time at which crystallization would have begun in the absence of undercooling). Draw AB through I parallel to the time axis. Draw a line through G and H intersecting AB at E and AC at D. Draw a line through H and I intersecting AC at J. Draw a line through J parallel to DE, intersecting AB at K. Draw a line through K and G, intersecting AC at F. F is the desired point, representing the freezing point of the given sample. Construction to determine t_{f_0}: Draw a line through G parallel to AB and a line through I parallel to AC, the two lines intersecting at L. Draw a line through points K and L, intersecting AC at M. M is the desired point, representing the freezing point for zero impurity, t_{f_0}.

VII. EVALUATION OF THE FREEZING POINT FROM A MELTING CURVE

Zero time is determined from a preliminary plot (as for the freezing curve) of the time-resistance observations covering the equilibrium portion of the melting curve and the liquid warming line, as shown in figure 7. Zero time can usually be determined by visual extrapolation, on this plot, of the equilibrium portion of the melting curve to its intersection with the liquid warming line extended down in tem-

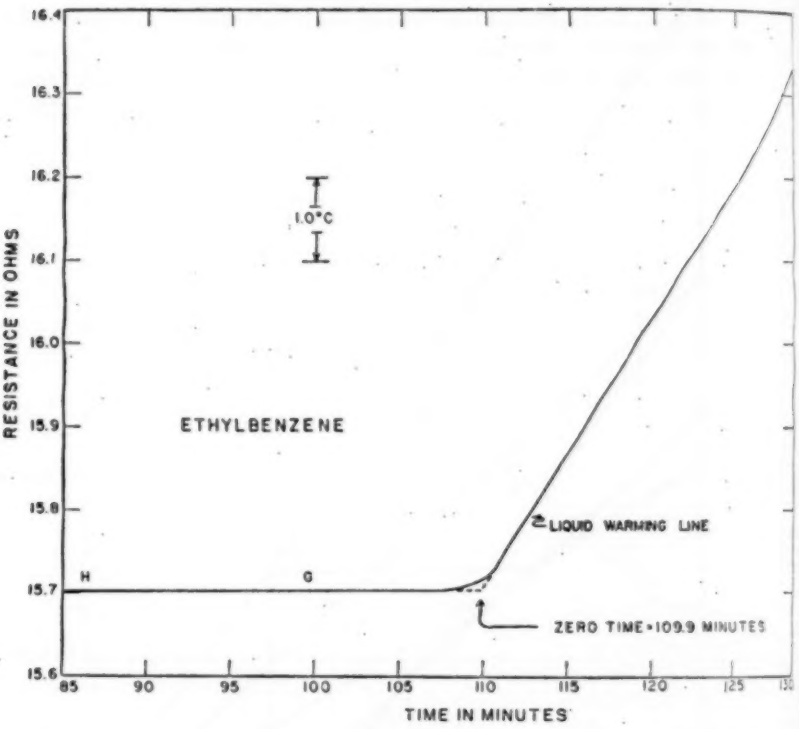

FIGURE 7.—*Time-temperature warming curve for determining "zero" time in an experiment on a sample of ethylbenzene.*

The scale of ordinates gives the resistance in ohms of the platinum resistance thermometer, and the scale of abscissas gives the time in minutes. HG represents part of the equilibrium portion of the melting curve. Zero time is given by the intersection of HG extended to its intersection with the backward extension of the liquid warming line. The same data are plotted in figure 8 with a magnified scale of temperature.

perature to its intersection with the extension of the equilibrium portion of the curve.

The location of the freezing point at F is done exactly as in the case of the freezing experiment, except that the geometrical construction is made to the right, as in figure 8. See figure 6 and reference [2] for details.

The conversion of resistance to temperature is made as previously described.

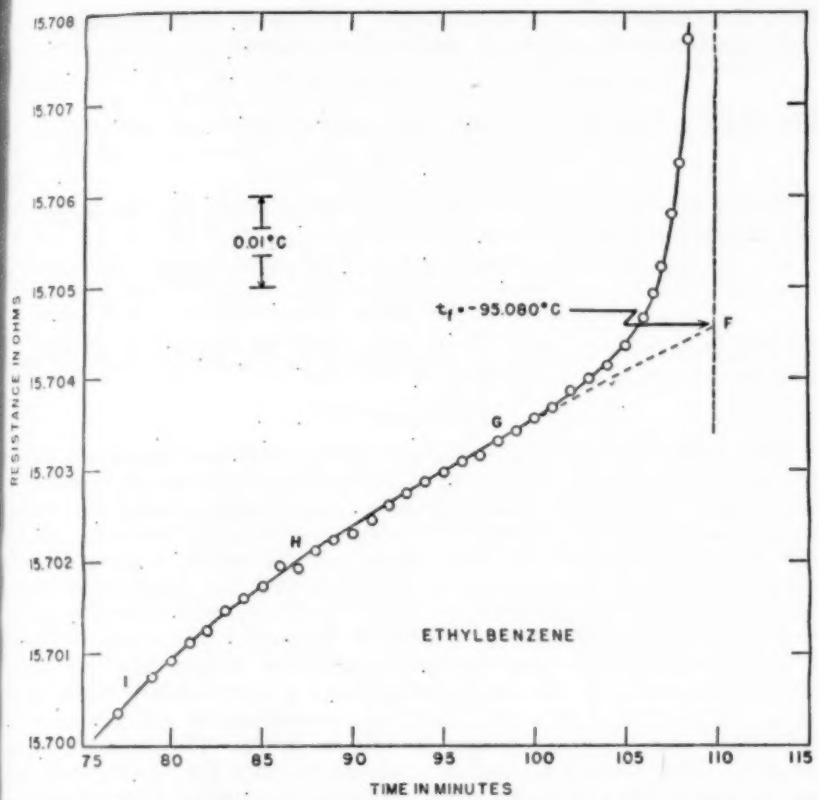

FIGURE 8.—*Time-temperature warming curve for determining the freezing point of a sample of ethylbenzene.*

The scale of ordinates gives the resistance in ohms of the platinum resistance thermometer, and the scale of abscissas gives the time in minutes. IHG represents the equilibrium portion of the melting curve. The freezing point F is determined as described in the text (see [2]). These data are the same as those plotted in figure 7.

VIII. CALCULATION OF THE PURITY WHEN THE FREEZING POINT FOR ZERO IMPURITY IS KNOWN

When the values of the freezing point for zero impurity and the cryoscopic constants are known, the measured value of the freezing point may be used to calculate the purity of the given sample by means of the equation

$$\log_{10} p = 2.00000 - (A/2.30259)(t_{f_0} - t_f)[1 + B(t_{f_0} - t_f)]. \qquad (7)$$

In eq 7, p is the purity in mole percent, t_f is the freezing point, t_{f_0} is the freezing point for zero impurity, and A and B are the cryoscopic constants [6] defined in section II.

For many hydrocarbons of low molecular weight, the value of the constant A lies in the range 0.005 to 0.06 deg^{-1} and that of the constant

[6] Selected "best" values of the cryoscopic constants of the more important hydrocarbons of the various classes are being compiled for publication in a joint investigation of the Thermochemical Laboratory and the American Petroleum Institute Research Project 44 at the National Bureau of Standards.

B in the range 0.000 to 0.005 deg^{-1}. In many cases, therefore, the constant B may be neglected, and eq 3 reduces to

$$\log_{10}p=2.00000-(A/2.30259)(t_{f_0}-t_f). \tag{8}$$

For small values of $t_{f_0}-t_f$, eq 8 reduces further to

$$p=100[1-A(t_{f_0}-t_f)]. \tag{9}$$

In terms of mole fraction of the major component, N_1, the equations corresponding to 7 and 9 are

$$\log_{10}N_1=-(A/2.30259)(t_{f_0}-t_f)[1+B(t_{f_0}-t_f)] \tag{10}$$

$$N_1=1-A(t_{f_0}-t_f). \tag{11}$$

In terms of mole fraction of the impurity, N_2, which is $1-N_1$, the limiting equation corresponding to eq 11 is

$$N_2=A(t_{f_0}-t_f). \tag{12}$$

The foregoing equations relating purity and temperature involve the two assumptions that all of the impurity in the given sample (a) remains in the liquid phase during crystallization, and (b) forms with the major component a substantially ideal solution. With regard to assumption (b), it is apparent that when a given hydrocarbon has been put through a logical system of purification there will remain as impurity only those hydrocarbons (usually close-boiling isomers) that are very similar to the major component. These latter hydrocarbons are, however, precisely those that are most likely to form with the major component a substantially ideal solution. With regard to assumption (a), involving the absence of solid solutions, the following points should be noted: The possible existence of solid solutions need be considered only for the case of the major component and its most probable impurities (usually close-boiling isomers); among hydrocarbons of low molecular weight, close-boiling isomeric impurities fortunately seldom possess the required shape and size of the molecule to favor the formation of solid solutions.

However, when there are known cases where a given hydrocarbon and its most probable impurity (for the given process of purification) form solid solutions, or otherwise do not conform to the requirements for the ideal relations, and if it is desired to translate into purity the freezing points of such systems, observations should be made on known mixtures of such hydrocarbons for the purpose of evaluating the actual relation between freezing point and purity. In general, in those cases where the identity of the impurity is known, the actual relation between purity and freezing point may be determined experimentally from known mixtures. In such cases, the observed relation, rather than the theoretically calculated relation for the ideal solution, should be used if the former is found to differ significantly from the latter.

IX. CALCULATION OF THE PURITY WHEN THE FREEZING POINT FOR ZERO IMPURITY IS NOT PREVIOUSLY KNOWN

When for the given compound under examination, the freezing point for zero impurity is not previously known, its value may be determined by application of the procedures previously described [1, 2].

The first of these procedures may be performed simply as follows: The time of crystallization is determined as described in part II–3 of reference [1]. If this experiment is not identical with the one from which the freezing point has been determined, the time of crystallization for the latter is related to that for the former (with the same quantity of sample in both experiments) as follows:

$$(z_{zln})_1/(z_{zln})_2=(\Delta t/\Delta z)_2/(\Delta t/\Delta z)_1, \tag{13}$$

where z_{zln} is the time of crystallization in minutes, $\Delta t/\Delta z$ is the cooling rate (or the negative of the warming rate) of the liquid phase at the freezing point in degrees per minute or ohms per minute, and the subscripts 1 and 2 identify the two experiments.[7]

Taking the rate of crystallization to be substantially constant [1], the fraction, r, crystallized at any time z_r is

$$r=(z_r-z_f)/z_{zln} \tag{14}$$

where z_f is "zero" time or the time at which crystallization begins (with no significant amount of undercooling). In the proper application of eq 9 and 10, it is necessary that the rate of introduction of energy by stirring be small in comparison with the total rate of heat flow to or from the sample.[8] If the stirring energy is significantly large, appropriate correction for it must be made in evaluating the time of crystallization, as described in part II–3 of reference [1]. The time z_r is selected as far as possible down the equilibrium portion of the curve (see GHI in fig. 5 and 8). Then the freezing point for zero impurity is

$$t_{f_0}=t_f+\left(\frac{1-r}{r}\right)(t_f-t_r), \tag{15}$$

where t_r is the equilibrium temperature at the time z_r. It is desirable to make the determination of t_{f_0} from several experiments on the same or different samples of the highest purity.

When the value of the freezing point for zero impurity is thus determined, and a value of the cryoscopic constant (or constants) is known, the calculation of the purity is made by means of the appropriate equations given in the preceding section.

Whenever the value of the cryoscopic constant A is not known, a value for it may be determined as described in the following section.

The second procedure for determining t_{f_0} is described on pages 205–207 of reference [2]. This procedure, which requires no additional experimental data, is applicable only to those experiments in which the time-temperature observations extend over a sufficiently large fraction (of the order of ¼ to ½) of material crystallized. The geometrical construction for determining t_{f_0} by this procedure is illustrated in figure 6. If the point M lies off the available plotting space,

[7] If the resistance-time curve at the freezing point, for either a melting or a freezing experiment, is not sufficiently linear to permit reasonably accurate evaluation of the slope directly from the resistance-time plot, the slope at the freezing point may be readily evaluated, from the data of either the freezing or the melting experiment, by plotting, as a function of time, values of the slope of successive chords of the resistance-time curve taken as the difference in successive readings of resistance divided by the time interval in minutes, and extrapolating these slopes to the "zero" time, z_f, at the freezing point.

[8] The energy of stirring may be readily determined by having the substance and container at the temperature of the jacket (0°, −80°, or −185° C), taking observations of resistance, with stirring, for a period of 10 minutes, stopping the stirrer for a period of 5 minutes, again taking observations of resistance, with stirring, for another period of 10 minutes, etc. The cessation of stirring in a given period produces, between the two periods adjacent to it, an offset (decrease) of the resistance (temperature) curve with respect to time. The actual displacement of the resistance-time line between the two stirring periods, measured at the middle of the period of no stirring, divided by 5, the number of minutes in which the stirrer was halted, gives the value of the stirring energy in terms of the change of resistance (temperature) per minute, of the given system.

its value may be determined analytically as follows [2]: Given the three points G, H, and I on the equilibrium curve, having values of time equal to z_G, z_H, and z_I (with point H having been selected midway between G and I in point of time, so that $z_G - z_H = z_H - z_I$) and values of temperature (resistance) equal to t_G, t_H, and t_I, respectively. Then (see footnote 5)

$$t_{f_0} = t_G + (t_G - t_I)/(u-1), \tag{16}$$

where

$$u = (t_H - t_I)/(t_G - t_H). \tag{17}$$

In general, it is desirable to utilize both of the foregoing procedures where possible. The two procedures should give the same result within the respective limits of uncertainty. (See fig. 5 in reference [2].)

X. DETERMINATION OF THE CRYOSCOPIC CONSTANT

When enough of the given compound is available, the cryoscopic constant may be determined directly by measuring the lowering of the freezing point caused by the addition to it of a measured amount of an appropriate solute. The amount of the given compound required is about 40 ml, and its purity should be about 97 or more mole percent. The solute required to be added is one that will form with the given compound a substantially ideal solution (with no solid solutions), its purity should be about 97 or more mole percent, and the amount required is about 2 ml. Preferably, the solute added should be isomeric with the given compound and the impurity in the solute should not include any significant amount of the given compound. Furthermore, the solute added must be one that does not form a eutectic mixture with the given compound at the resulting concentration in the solution formed. In general, eutectic mixtures of this low concentration will be likely to occur only for solutes that have freezing points much higher than the given substance.[9]

Let H be the given hydrocarbon compound under examination. Measurement is made of the freezing point, t_f^p, of a sample of "pure" H, according to the procedure described in the preceding sections of this report. To a weighed amount of 40 ml of pure H is added 2 ml of the given solute, with the weight of the solute being determined from the increase in weight. The solution thus formed is one in which the concentration of the hydrocarbon H is about 5 mole percent less than in the pure H. Measurement is made of the freezing point, t_f', of the solution. Let

m^p = the mass of the pure H used in making the solution of H.
m^q = the mass of the solute, Q.
M^p = the molecular weight of pure H, taken to be that given by the molecular formula of H;
M^q = the molecular weight of the solute, Q, taken to be that given by the molecular weight of Q;
N^p = the mole fraction of H in pure H;
N' = the mole fraction of H in the solution formed from H and Q, calculated from the masses and molecular weights. If H and Q are isomeric, the mole fraction is identical with the weight fraction.

[9] For example, *p*-xylene (fp = 13.26° C) forms with ethylbenzene (fp = −94.95° C) a eutectic mixture in which there is about 3½ mole percent of *p*-xylene.

Then the following relations hold

$$-\ln N^p = A(t_{f_0} - t_f^p) \tag{18}$$

$$-\ln N^s = A(t_{f_0} - t_f^s) \tag{19}$$

$$-\ln (N^s/N^p) = A(t_f^p - t_f^s) \tag{20}$$

$$A = -2.3026\ [\log_{10} (N^s/N^p)]/(t_f^p - t_f^s). \tag{21}$$

For many compounds, the value of $t_f^p - t_f^s$ in the foregoing experiments will be, for the amounts indicated, about 1° to 2° C, and the uncertainty in the resulting value of the cryoscopic constant should be not more than several percent. (See reference [3]).

In case 40 ml of the given compound in a purity of about 97 percent is not available for making up a solution as described above, the cryoscopic constant, A, may be determined, without contaminating the sample, from a value of the heat of fusion estimated by a comparison with observations on a substance whose heat of fusion is known [1]. The procedure is as follows: Select a similar compound F whose heat of fusion is known and whose freezing point is within about 15° C of that of the compound G whose heat of fusion is to be estimated. Perform a complete time-temperature freezing experiment on the substance F, and likewise on the substance G, using substantially the same number of moles in each case and the same jacket temperature. For each of the experiments, the corrected time of crystallization is determined. Then, approximately,

$$(\Delta Hm)_G = (\Delta Hm)_F \frac{(\Delta t/\Delta z)_G (z_{xln})_G}{(\Delta t/\Delta z)_F (z_{xln})_F}. \tag{22}$$

The foregoing relation will yield a value for the heat of fusion, and hence the cryoscopic constant, which will in most cases be uncertain by not more than about 20 percent of itself. The accuracy of this procedure can be improved by using two reference substances, one of freezing point above and the other below that of the given substance, and appropriately interpolating.

Where possible, the method of determining the cryoscopic constant by direct measurement of the lowering of the freezing point is to be preferred over the approximate method described in the preceding paragraph. For use in the ideal systems discussed in this report, the most accurate values of the cryoscopic constants are usually derived from heats of fusion measured calorimetrically.

XI. DISCUSSION

Duplicate determinations of the freezing point of a given sample made by a given operator with the apparatus and procedure described in sections III to VII will usually differ by not more than 0.002 to 0.005 degree centigrade, except for very impure samples and for compounds having rather small values of the cryoscopic constant A. It follows that duplicate determinations would yield values of purity (in mole percent) differing usually by not more than 0.2 to 0.5 times the cryoscopic constant A (in deg^{-1}).

Determinations of the freezing point of a given sample made in different laboratories with the apparatus and procedure described in sections III to VII should normally differ by not more than about 0.01 to 0.02 degree centigrade, if the resistance bridges and the plati-

num resistance thermometers have been properly calibrated, as with constants certified by the National Bureau of Standards, and measurements of the ice point are made at appropriate intervals.

Assuming that the impurity remains entirely in the liquid phase during crystallization and forms with the major component a substantially ideal solution, the uncertainty in the value of the purity of a given sample determined with the present apparatus and procedure will include (a) an uncertainty in the value of the freezing point t_0 which uncertainty has been discussed above, and (b) an uncertainty in the given value of t_{f_0}. For substances having a large value of the cryoscopic constant A, the uncertainty in t_{f_0} will usually be near 0.01 to 0.03 degree centigrade, if the sample available for measurement has a purity of about 99.8 or more mole percent. For substances having a small value of the cryoscopic constant A, the uncertainty in t_{f_0} may be near 0.05 to 0.10 degree centigrade, when the determination is made on a sample having a purity of about 99.8 or more mole percent. The uncertainty in the value of t_{f_0} will, of course, decrease with increase in the purity of the sample. As discussed in section VIII, calculations relating to systems of known components should be based, when possible, upon actual experimental observations on known mixtures of such compounds.

For those compounds that have one or more metastable forms whose freezing points can be determined, it becomes necessary to ascertain for which crystalline form the determined freezing point has been obtained. For those cases where the freezing point (for zero impurity) of metastable form II is more than a few degrees below that of the stable form I, there is little difficulty in identifying the forms, as it would usually require a rather impure sample of form I to have a freezing point below that of a pure sample of form II. When the difference in the freezing points (for zero impurity) of the two forms is less than several degrees, and especially when the difference is less than one degree, the problem of identifying the forms is somewhat more involved. However, except in the most complicated case, it is possible to determine the value of t_{f_0} yielded by the given experiment (as outlined in section IX) and to identify the crystalline form from the value of t_{f_0}.

Measurements of freezing points of actual "best" samples, with evaluation of freezing points for zero impurity, together with determinations of cryoscopic constants as required, have been made, according to the method and procedures described in this report, on approximately 80 different purified hydrocarbons of the paraffin, alkylcyclopentane, alkylcyclohexane, alkylbenzene, monoolefin, diolefin, and cyclomonoolefin series in connection with the work at this Bureau of the American Petroleum Institute Research Project 6 on the purification and properties of hydrocarbons. Determinations of the purity of the NBS Standard Samples of hydrocarbons are also being made by the procedures described in this report. Complete details of this experimental work will appear in other reports from the National Bureau of Standards [7].

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U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1677

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EFFECT OF PRESSURE ON THE MELTING OF CRYSTALLINE RUBBER[1]

By Lawrence A. Wood, Norman Bekkedahl, and Ralph E. Gibson[2]

ABSTRACT

The effect of hydrostatic pressure on the melting of crystalline rubber has been the subject of a brief investigation extending to pressures above 1,000 atmospheres. With a particular sample of stark rubber, it was found possible to raise the temperature of melting, as determined by the disappearance of birefringence, from about 36° to 70° C by the application of a pressure of 1,170 bars ($1{,}170 \times 10^6$ dynes/cm^2). The results, including observations at intermediate pressures, can be represented adequately by the equation $\log_{10}(p+1{,}300) = 5.9428 - (875/T)$.

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I. INTRODUCTION

The effect of hydrostatic pressure on the melting of crystalline rubber has been the subject of a brief investigation extending to pressures above 1,000 atmospheres. With a particular sample of stark rubber it was found possible to raise the temperature of melting as determined by the disappearance of birefringence, from about 36° to 70° C by the application of a pressure of 1,170 bars ($1{,}170 \times 10^6$ dynes/cm^2). The results, including observations at intermediate pressures, are given in table 1 and in figure 1.

II. SAMPLE

The crystalline smoked-sheet sample, called stark rubber, as it had a melting range above room temperature, was furnished in 1939 by H. I. Cramer while he was a professor at the University of Akron.

Melting of a portion of this sample at atmospheric pressure was determined from observations of volume changes in a mercury-filled dilatometer by a method previously described [1, 2].[3] It can be seen from the temperature-volume relation shown in figure 2 that the melting occurred over a range of temperature from 32° to 39° C.

[1] Also appears in J. Chem. Phys. 13, 475 (1945).
[2] At the time this work was done, Dr. Gibson was a member of the staff of the Geophysical Laboratory of the Carnegie Institution of Washington.
[3] Figures in brackets indicate the literature references at the end of this paper.

The disappearance of the birefringence, which according to figure 1 takes place close to 36° C at atmospheric pressure, evidently defines a position near the center of the melting range.

The expansivity $(1/V)(dV/dT)$ at 25° C of the amorphous rubber calculated from data plotted in figure 2 is found to be 650×10^{-6} per degree centigrade and that of the crystalline rubber 590×10^{-6} per degree centigrade.

III. APPARATUS AND PROCEDURE

The high-pressure equipment used in this investigation was located in the Geophysical Laboratory of the Carnegie Institution of Washington and has been described in previous papers [3, 4]. The approximate adjustment of the pressure was made by means of a hand pump and the fine adjustment by a screw plunger operated by a wheel. The amount of pressure was determined by a calibrated manganin wire resistance-gage [5, 6].

Specimens of the stark rubber sample were cut into strips about a millimeter in thickness. One strip of this stark rubber, together with a similar strip previously melted by heating to about 70° C, was placed side by side in a glass piezometer. The use of two specimens adjacent to each other permitted an excellent visual criterion for determining when birefringence disappeared.

Ethylene glycol was used as a confining liquid in the piezometer. Water was found to be unsatisfactory for this purpose as it penetrated the rubber specimens and impaired their transparency after several hours at high pressures. No such difficulty was encountered with the ethylene glycol.

Light from a 6-volt, 32-candlepower lamp, after being polarized by a sheet of Polaroid, passed through the window of the pressure equipment and through the specimen. The polarized light was observed, after emerging from the equipment, by the use of a second sheet of Polaroid as analyzer.

In operation, the piezometer containing the specimens was placed in the apparatus, the pressure increased to about 1,300 bars, and the temperature of the bath raised to the desired value. After temperature equilibrium was attained, the pressure was slowly lowered and continuous observations made of the birefringence. Except during the melting of the stark specimen, no significant variation with pressure was noted in the appearance of the birefringence of the two specimens between crossed Polaroids.

IV. RESULTS AND DISCUSSION

The change in birefringence associated with the melting of the stark specimen was found to take place over a small range of pressure, with the major portion of the change occurring within an interval of only a few bars. The pressure at which the change of birefringence was most rapid has been used as abscissa in figure 1, and the corresponding bath temperature used as ordinate. A new specimen, cut from the same sheet of stark rubber, was required for each point. The data from which the curve was plotted are given in the first two columns of table 1.

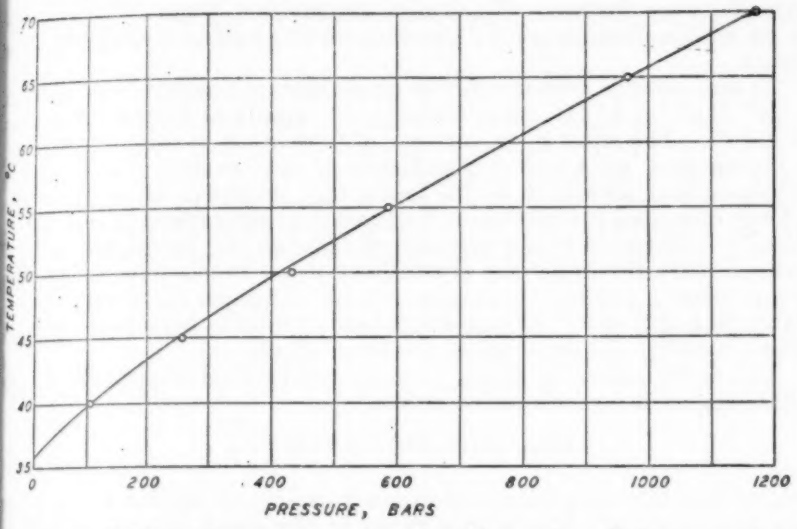

FIGURE 1.—*Relation between temperature of melting and applied pressure for a sample of stark rubber.*

TABLE 1.—*Pressure and related quantities at temperature of melting*

Temperature of melting	Pressure		dT/dp calculated	$L/\Delta V$, calculated
	Observed	Calculated		
°C	*Bars*	*Bars*	*deg C/bar*	*j/cm³*
36.2	----------	1	0.0365	846
40	106	108	.0345	906
45	259	258	.0323	987
50	433	419	.0302	1,060
55	586	590	.0283	1,160
65	967	966	.0250	1,350
70	1,170	1,172	.0236	1,450

The relation between the temperature of melting and the pressure shown by the curve cannot be regarded as valid for crystalline rubber having at atmospheric pressure a melting range different from that described here. As the melting range at atmospheric pressure is dependent on the temperature at which the crystals were formed [7], this fact limits the application of the present results. However, if a study were to be made of rubber crystallized at different temperatures, it is presumed that as a first approximation a family of curves not too far from parallel would be obtained with displacement along the temperature axis.

Some crystallization was observed when amorphous specimens were kept under a pressure of about 1,100 bars at 30° C for 16 hours. It was observed that the crystals formed in this manner melted at a much lower temperature than the value for the same pressure given by the curve in figure 1. The crystals formed under these conditions were evidently different from those present originally in the stark rubber. At atmospheric pressure the temperature of melting, as already mentioned, is dependent on the temperature at which the

crystals were formed. No doubt the melting depends in a somewhat similar fashion on the pressure on the rubber during crystallization.

At atmospheric pressure rubber crystallizes at temperatures between −50° C and +15° C, crystallizing most rapidly at temperatures near −25° C. The effect of an increase of pressure is to raise the range of temperatures at which crystallization may occur. For example, Thiessen and Kirsch [8, 9, 10] found that pressures up to 25 atmospheres increased the rate of crystallization at temperatures near 10° C. Dow [11] observed that a pressure of 8,000 kg/cm² raised the range of temperature favorable for crystallization so much that no crystals were formed during 14 days at 0° C. The partial crystallization after 16 hours at 30° C under a pressure of 1,100 bars in the present work is additional evidence of the same effect.

The curve shown in figure 1 can be represented adequately by the three-constant logarithmic equation,

$$\log_{10}(p+1{,}300)=5.9428-\frac{875}{T},$$

where T is the temperature of melting in degrees Kelvin and p is the pressure in bars. The values given in the third column of table 1 are calculated from the above equation. A differentiation of the equation gives

$$\frac{dT}{dp}=\frac{T^2}{2{,}015\ (p+1{,}300)},$$

from which the values in the fourth column of the table were calculated.

The use of the Clapeyron equation,

$$\frac{dp}{dT}=\frac{L}{T\Delta V},$$

where L is the heat of fusion and ΔV the corresponding change in volume, permits a calculation of $L/\Delta V$ from the data just given. This quantity, in joules per cubic centimeter of volume change, is shown in the last column of the table.

From the dilatometric measurements represented by the graph in figure 2, ΔV was found to be 0.0191 cm³/g of rubber at 36.2°C. From these data the value of L for this sample is calculated to be 16.2j g.

Other observations in this laboratory have shown that this sample of stark rubber could undergo additional crystallization at lower temperatures. The full heat of fusion should include the contribution of these additional crystals, which were observed to form at the lower temperatures. Therefore, we do not regard the value just given as the full heat of fusion of crystalline rubber at 36.2° C. A direct measurement [12] of the heat of fusion of another sample of rubber melting over a range centered at about 11° C yielded 16.7 j g. The corresponding value at 36.2° C might be expected to be larger than that at 11° C. The term ΔV and T in the Clapeyron equation are both larger at the higher temperature, but a lack of data regarding the values of $(dp)/(dT)$ at 1 bar for samples melting between 11° and 36.2° C prevents drawing a definite conclusion. In spite of the impossibility of making an exact calculation with the data available, the agreement in order of magnitude is quite satisfactory.

The rate of change of melting temperature with pressure is observed to have the value of 0.037 degree centigrade per bar at the lowest pressures and to decrease with increasing pressure to a value of about 0.024 degree centigrade per bar at 1,170 bars. The average value over the range studied is 0.029 degree centigrade per bar. This is considerably lower than the average value calculated from a single observation of Dow [11], who found rubber crystallized at 0° C to melt at 77.5° C under a pressure of 1,270 kg/cm². From this observation one may calculate a value of 0.052 degree centigrade per bar if 11° C is taken as the melting temperature at atmospheric pressure for rubber crystallized at 0° C [1].

The experimental observations for the present investigation were made in the summer of 1940, but earlier publication was prevented by war activities, which also led to the abandonment of a more extensive investigation that had been planned.

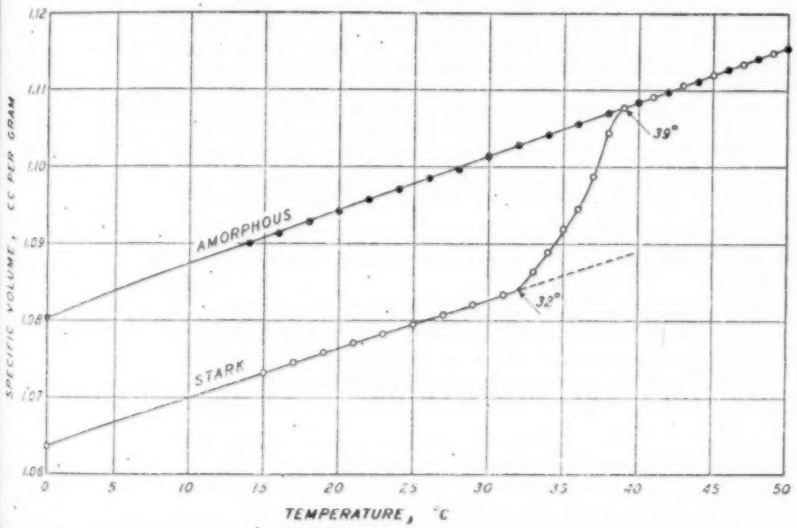

FIGURE 2.—*Relation between specific volume and temperature at atmospheric pressure for the sample of stark rubber, before and after melting.*

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RESEARCH PAPER RP1678

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SECOND DISSOCIATION CONSTANT OF *o*-PHTHALIC ACID AND RELATED pH VALUES OF PHTHALATE BUFFERS FROM 0° TO 60° C

By Walter J. Hamer and S. F. Acree

ABSTRACT

Measurements were made of the potential difference between hydrogen electrodes and silver–silver-chloride electrodes in aqueous solutions of 72 different phthalate-chloride mixtures at 13 temperatures from 0° to 60° C. By described experimental and mathematical procedures, the second dissociation constant of *o*-phthalic acid and related thermodynamic quantities were evaluated, and pH values were assigned to 217 solutions, including some containing no potassium chloride. The addition of the chloride lowers the pH of the solutions principally because of an increase in the ionic strength.

The second dissociation constant may be computed at each temperature by the equation

$$\log K_2 = -2175.83/T + 9.55095 - 0.025694T,$$

where $T = t\,^{\circ}\mathrm{C} + 273.16$.

The pH values of the solutions may be computed for ratios of dipotassium phthalate to acid potassium phthalate from 1 to 2, and for ionic strengths, μ, from 0 to 0.5, by the equation

$$\mathrm{pH} = -\log K_2 + \log \frac{\text{dipotassium phthalate}}{\text{acid potassium phthalate}} - 3A\sqrt{\mu}/(1 + 3.76B\sqrt{\mu}) + \beta\mu,$$

in which A and B are constants dependent upon the temperature, and β is a constant dependent upon the temperature, salt concentration, and buffer ratio.

The addition of potassium chloride lowers the pH of the solutions in accordance with the equation

$$\mathrm{pH} = (\mathrm{pH})_0 + \alpha_1 m_{\mathrm{KCl}} + \alpha_2 m^3_{\mathrm{KCl}} + \alpha_3 m^5_{\mathrm{KCl}},$$

where $(\mathrm{pH})_0$ is the value at any temperature for a solution containing no potassium chloride and α_1, α_2, and α_3 are constants.

These solutions with or without potassium chloride are useful as pH standards from 4.87 to 5.72 and vary only slightly with changes in temperature. They have good buffer capacity and may be readily prepared from pure materials. The NBS Standard Samples 84a and 84b of acid potassium phthalate or Standard Samples of comparable purity are recommended for preparation of the solutions, together with carbonate-free potassium hydroxide of high grade and distilled water of pH 6.7 to 7.3.

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I. INTRODUCTION

Precision pH standards may be defined as buffer solutions whose compositions can be accurately reproduced and the pH values accurately obtained by hydrogen-electrode measurements. The pH standards commonly used are prepared from a weak acid and its salt, such as acetic acid and sodium acetate, or by the neutralization of an acid with alkali. The ideal ones can be prepared directly from a single salt, preferably a salt that is easily purified and is neither hygroscopic nor deliquescent, such as acid potassium phthalate. This salt is now issued by the National Bureau of Standards for acidimetric work and may be used equally well as a pH standard.

Mixtures of acid potassium phthalate with hydrochloric acid or with sodium hydroxide were included in a list of standards for hydrogen-ion determination prepared by Clark and Lubs [1][1] in 1916. They determined the pH of the solutions by a galvanic cell comprised of a hydrogen electrode, a salt bridge of saturated potassium chloride, and a decinormal calomel half-cell. For many years after their measurements, the reproducibility of hydrogen electrodes in solutions of acid potassium phthalate was questioned. Many experimenters found drifting potentials with hydrogen electrodes. However, it has been recently found that hydrogen electrodes prepared with palladium function well and that precise values of the pH of phthalate solutions can be obtained with their use [2]. Clark and Lubs chose 0.3379 v for the potential of their calomel half-cell at 20° C and assumed that the potentials at the junctions of the saturated potassium chloride bridge with the phthalate solution and the 0.1-*N* potassium chloride were zero. By this procedure, they obtained 3.974 for the pH of a 0.05-*M* solution of acid potassium phthalate. However, the liquid-junction potentials are not zero. For instance, the potential for the junction between 0.1-*N* and saturated potassium chloride is 0.00187 v at 25° C [3]. A value of 0.00251 v may be calculated by the Henderson equation [4] for the potential of the junction between saturated potassium chloride and 0.05-*M* acid potassium phthalate, if 50.5 is used for the mobility of the acid phthalate ion. These values with 0.3337 v [3] for the potential of the 0.1-*N* calomel half-cell excluding liquid-junction potentials give 0.3343 v for the value of the total calomel half-cell and bridge. Many other values for this half-cell, and, therefore, for the pH of 0.05-*M* acid potassium phthalate, have been suggested from time to time.

The problem of determining pH values from the emf of cells with liquid junction becomes more perplexing when it is realized that the potential of a liquid junction cannot be determined on a thermodynamic basis without assumptions regarding the magnitude of the activity coefficients of the individual ions involved at the liquid junction, and that the potential of a liquid junction depends upon the manner in which it is constructed. Clark and Lubs assumed that the hydrogen electrode gives a measure of hydrogen-ion concentration,

[1] Figures in brackets indicate the literature references at the end of this paper.

whereas in reality it gives a measure of hydrogen-ion activity. In order to establish a pH scale on the basis of hydrogen-ion activity, Hitchcock and Taylor [5] and MacInnes, Belcher, and Shedlovsky [6] calibrated the calomel half-cell with solutions whose properties had been determined by cells without liquid junction.[2] The former obtained 0.2441 v for the saturated calomel half-cell and the latter 0.3360 v for the decinormal calomel half-cell. With the use of these values, they calculated 4.008 and 4.000, respectively, for the pH of 0.05-*M* acid potassium phthalate at 25° C. Recently, Hamer and Acree [9] obtained a value 4.008 for this solution by an abbreviated method based upon the measurements of galvanic cells without liquid junction.

A more precise method of approach to this problem is to make a comprehensive study of the thermodynamics of acid potassium phthalate or of mixtures of *o*-phthalic acid and potassium hydroxide. From the known equilibria of the two ionization steps in the dissociation of *o*-phthalic acid, designated as H_2Ph, and the concentration of the acid (a) and added base (b), it may be shown that the hydrogen-ion concentration of acid potassium phthalate of any strength ($a=b$ in this case) is given by eq 1:

$$H^3+[a+(K_1f_{H_2Ph})/(f_Hf_{HPh})]H^2+[(K_1K_2f_{H_2Ph})/(f^2{}_Hf_{Ph})]H-(aK_1K_2f_{H_2Ph})/(f^2{}_Hf_{Ph})=0, \quad (1)$$

on the reasonable assumption that the effects of hydrolysis are small. Therefore, in order to obtain the true value of the hydrogen-ion concentration of acid potassium phthalate of any concentration, it is necessary to obtain precise values of the dissociation constants, K_1 and K_2, and of the activity coefficients, f, of the various ionic species.[3]

This paper gives the results of measurements of galvanic cells without liquid junctions and with hydrogen and silver–silver-chloride electrodes for the determination of K_2, the related activity coefficients, and the pH values of the solutions used in the determination of K_2. Measurements were made at 5-degree intervals from 0° to 60° C, inclusive, in order to determine the pH values over this range of temperature and to determine several thermodynamic quantities for the process $HPh^-=H^++Ph^=$. By comparison of these quantities with similar ones for other and similar types of dissociation, a critical estimate may be made of the reliability of the values of K_2. Determinations of K_2 were made prior to K_1 because the low solubility of *o*-phthalic acid prevents an accurate evaluation of the ionic sizes and "salting-out" coefficients of phthalate ions.

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[2] It is well known that an exact differentiation between hydrogen-ion concentration and activity cannot be made, as the value of the activity coefficient of the hydrogen ion cannot be determined without some assumption. Hitchcock and Taylor, and MacInnes, Belcher, and Shedlovsky in their method obtain a quantity that approximates the value of the hydrogen-ion activity. In this paper the assumption is made that the activity coefficients of ions are given by the Hückel equation and that the "salting-out" terms of the chloride and hydrogen ions are equal. See references [3, 7, 8] for discussions of assumptions used in connection with work on measurements of acidity.

[3] In this paper, the symbol f is used for the activity coefficient of an ion or molecule for any scale of concentration. In this work, molality is used as the concentration unit. The symbol γ is often used for activity coefficients on this scale of concentration.

II. METHOD FOR THE DETERMINATION OF THE SECOND DISSOCIATION CONSTANT OF o-PHTHALIC ACID

1. APPROXIMATE METHOD[4]

In the determination of the second dissociation constant of o-phthalic acid by the electromotive-force method, measurements are made of the emf of the galvanic cell

$$\text{Pd, } H_2(g)|KHPh(m_1),\ K_2Ph(m_2),\ KCl(m_3)|AgCl(s)|Ag(s) \quad (1)$$

for a series of solutions of different molalities, m_1, m_2, and m_3, and of various buffer ratios, $K_2Ph/KHPh$, wherein the hydrogen and silver-silver-chloride electrodes are reversible, respectively, to hydrogen and chloride ions. The addition of the chloride is therefore a prerequisite for the use of silver–silver-chloride electrodes in such solutions. The calculations of the constant depend upon the equation[5]

$$E=E^\circ-(RT/F)\ln(a_Ha_{Cl})=E^\circ-(RT/F)\ln a_H-(RT/F)\ln(f_{Cl}m_{Cl}), \quad (2)$$

relating the emf of the cell, E, with the activities of the hydrogen and chloride ions, and upon the mass-action expression

$$K_2=(a_Ha_{Ph})/a_{HPh}=(a_Hf_{Ph}m_{Ph})/(f_{HPh}m_{HPh}), \quad (3)$$

which defines the dynamic equilibrium between the ions for the process $HPh^-=H^++Ph^=$. E° is the potential of the silver–silver-chloride electrode for unit activity of hydrochloric acid; a, f, and m are the activity, activity coefficient, and molality of the ions denoted by subscripts; and R, T, and F have their usual significance. In eq 2 and 3, E, E°, m_{Ph}, m_{HPh}, m_{Cl}, R, T, and F are known quantities, whereas a_H and the activity coefficient terms (f) are unknown quantities. The former unknown may be eliminated by combining eq 2 and 3 to give

$$[(E-E^\circ)/(2.3026RT/F)+\log(m_3m_1/m_2)]+\log(f_{Cl}f_{HPh}/f_{Ph})=-\log K_2=pK_2, \quad (4)$$

upon substitution of m_1, m_2, and m_3, respectively, for HPh^-, $Ph^=$ and Cl^-.

The last term on the left side of eq 4 is an unknown quantity. The values of the activity coefficients in this term give the magnitude of the deviations of the ions or molecules from the perfect state. If the ions in solution conformed to the laws of perfect solutes having unit activity coefficients, this term would be zero. Only at infinite dilution do ions possess the characteristics of ideal solutes. Hence if values of the term in brackets for decreasing values of (m_3m_1/m_2) are plotted against the ionic strength, values of pK_2 are obtained by

[4] A review of the development of the method and its application to a large number of acids and bases is given by Harned and Owen [10]. Heretofore, a successful application of the method to dibasic acids for which the ratio of the second to the first dissociation constant is greater than 10^{-3} has not been made (see Glasstone, Introduction to electrochemistry, p. 322, D. Van Nostrand Co., Inc., New York, N. Y., 1942), and involves successive approximations, which are tedious. The ratio of the constants for o-phthalic acid is about 3×10^{-3}, and hence the present paper presents the application of the method to a more involved system. For a review of earlier emf studies of the ionization of weak electrolytes, see references [11, 12].

[5] For simplicity, the ionic charges are omitted in the formulas and equations.

extrapolation to zero ionic strength. This extrapolation is usually difficult, owing to a marked curvature in the plots in the range of concentration accessible to experimental measurements [8]. However, this difficulty may be overcome by the use in eq 4 of the Debye-Hückel equations [13, 14] for the activity coefficients of the ions. From theoretical considerations Debye and Hückel obtained eq 5,

$$-\log f_i = Az_i^2\sqrt{\mu}/(1+Ba_i\sqrt{\mu})+\beta m_i, \tag{5}$$

for the activity coefficient of an ion in terms of the general constants A and B, the constants a_i and β characteristic of the electrolyte under consideration, the ionic charge, z_i, the ionic strength of the solution, μ, expressed in moles of solute per liter of solution, and the concentration of ions (or salt).[6] For the HPh^-, $Ph^=$, and Cl^- ions, this equation gives

$$-\log f_{HPh} = A\sqrt{\mu}/(1+Ba_i\sqrt{\mu})+\beta_{HPh}m_{HPh}, \tag{6}$$

$$-\log f_{Ph} = 4A\sqrt{\mu}/(1+Ba_i\sqrt{\mu})+\beta_{Ph}m_{Ph}, \tag{7}$$

$$-\log f_{Cl} = A\sqrt{\mu}/(1+Ba_i\sqrt{\mu})+\beta_{Cl}m_{Cl}. \tag{8}$$

Substitution of these expressions in eq 4 for the respective activity coefficients gives eq 9,

$$(E-E^\circ)/(2.3026RT/F)+\log(m_3m_1/m_2)+2A\sqrt{\mu}/(1+Ba_i\sqrt{\mu}) -\beta_{HPh}m_{HPh}+\beta_{Ph}m_{Ph}-\beta_{Cl}m_{Cl}=-\log K_2=pK_2. \tag{9}$$

The term $(-\beta_{HPh}m_{HPh}+\beta_{Ph}m_{Ph}-\beta_{Cl}m_{Cl})$ may be replaced by $\beta\mu$. Justification of this may be shown as follows. If the properties of each ionic specie present in the mixture are additive functions of those of the individual ions composing the mixture, then $\beta_{Ph}m_{Ph}-\beta_{HPh}m_{HPh}-\beta_{Cl}m_{Cl}$ would equal $1/2(\beta_{Ph})\mu_{Ph}-\beta_{HPh}\mu_{HPh}-\beta_{Cl}\mu_{Cl}$ as $\mu_{Ph}=2m_{Ph}$, $\mu_{HPh}=m_{HPh}$, and $\mu_{Cl}=m_{Cl}$, and $\mu=\mu_{Ph}+\mu_{HPh}+\mu_{Cl}$. Now, if the ionic strength due to each ion is some fraction of the total ionic strength, namely, $\mu_{Ph}=p\mu$, $\mu_{HPh}=q\mu$, and $\mu_{Cl}=r\mu$ where p, q, and r are constants for a specified ratio of salts, we have $1/2(p\beta_{Ph})\mu-(q\beta_{HPh})\mu-(r\beta_{Cl})\mu=1/2(p\beta_{Ph}-2q\beta_{HPh}-2r\beta_{Cl})\mu=\beta\mu$. Hence the substitution of $\beta\mu$ for the term $(-\beta_{HPh}m_{HPh}+\beta_{Ph}m_{Ph}-\beta_{Cl}m_{Cl})$ is justified. With this substitution, eq 9 becomes

$$[(E-E^\circ)/(2.3026\ RT/F)+\log(m_3m_1/m_2)+2A\sqrt{\mu}/(1+Ba_i\sqrt{\mu})]+\beta\mu=-\log K_2=pK_2 \tag{10}$$

$$pK_2'+\beta\mu=pK_2 \tag{10a}$$

where pK_2' is used to designate the terms in the brackets of eq 10. Values of pK_2 are then obtained by extrapolation to infinite dilution of the values of pK_2' as a function of μ. The negative of the slopes of these plots gives the values of β for the various ratios of salts used in the experiments.

As values of p, q, and r are known for each ratio of salts, the values of β_{Ph}, β_{HPh}, and β_{Cl} may be determined from the observed values of β as the ratio of salts is altered. It should be noted that when all three salts are kept in constant ratio, values of p, q, and r remain the same

[6] Scatchard [15] recommends the use of molality, or moles of solute per 1,000 g of solvent, in the Debye-Hückel equation. This recommendation has been followed in this laboratory.

even if the concentration of each salt varies considerably. However, values of p, q, and r vary if the ratio of only two salts is kept constant. Hence, it is simpler to use the molalities of each ionic species than values of p, q, and r in the calculations. When the molalities of each ionic species are used, a series of simultaneous equations of the type $(\beta_{Ph}m_{Ph}-\beta_{HPh}m_{HPh}-\beta_{Cl}m_{Cl}=\beta\mu)$ are obtained, from which the values of β_{HPh}, β_{HPh}, and β_{Cl} may be evaluated. In the present case the simultaneous equations were solved by the method of least squares.

It is then possible by using these individual β values to calculate the pH values of the different solutions by means of eq 2 or the expanded form of eq 3, namely,[7]

$$(E-E^\circ)/(2.3026\ RT/F)+\log m_{Cl}-A\sqrt{\mu}/(1+Ba_i\sqrt{\mu})+\beta_{Cl}m_{Cl}=-\log a_H=\text{pH}; \tag{11}$$

$$pK_2-\log(m_1/m_2)-3A\sqrt{\mu}/(1+Ba_i\sqrt{\mu})+\beta_{Ph}m_{Ph}-\beta_{HPh}m_{HPh}=-\log a_H=pH. \tag{12}$$

Frequently the hydrogen-ion concentration is also desired (see footnote 2). If it is assumed that $\beta_H=\beta_{Cl}$, the hydrogen-ion concentration may be computed [16] from the emf by the equation

$$(E-E^\circ)/(2.3026\ RT/F)+\log m_{Cl}-2A\sqrt{\mu}/(1+Ba_i\sqrt{\mu})+\beta_{Cl}m_{Cl}+\beta_H m_H=-\log m_H. \tag{13}$$

This equation is used in the calculation of m_H, needed for the more rigorous evaluation of K_2 described below.

In the above procedure, the terms involving β for the various ions were considered to be additive. This procedure may be justified as follows, from considerations of the activity coefficients of hydrochloric acid in acid-salt mixtures. Güntelberg [17] and Harned [18] have shown that the activity coefficient of hydrochloric acid in acid-salt mixtures of a constant total molality is given by the relationship

$$\log(f_H f_{Cl})_{\text{mixture}}=\log(f_H f_{Cl})_{\text{pure}}-k_1 m_{\text{salt}}, \tag{14}$$

where k_1 is a constant dependent upon the total molality of the mixture, and $(f_H f_{Cl})_{\text{pure}}$ is that for the total molality of the mixture. For mixtures of hydrochloric acid and potassium chloride at 25°C k_1=0.080 and 0.0624 for a total molality, respectively, of 0.1 and 0.5. For aqueous solutions of pure hydrochloric acid, Harned and Ehlers [19] obtained the expression [8] (eq 15) for the activity coefficient as a function of

$$\log(f_H f_{Cl})_{\text{pure}}=-A\sqrt{\mu}/(1+Ba_i\sqrt{\mu})+0.133\mu \tag{15}$$

the molality at 25° C. Hence, for an ionic strength of 0.1,

[7] In the above treatment, a_i is considered to be the same for each ion. This constant has the dimensions of reciprocal centimeters and represents the so-called closest distance of approach of the ions in solution. On the other hand, the value of a_i could be considered an average of different values for the various ions. If this were the case, a different value of a_i would be required in eq 9 for different buffer ratios. The individual values of the closest distance of approach of each ion could then be determined by the method of simultaneous equations, using the relationship $a_{av}=a_1m_1+a_2m_2+a_3m_3$ or some other more complex function, where a_i is the observed value for different buffer ratios and a_1, a_2, and a_3 represent, respectively, the closest distance of approach of the acid phthalate, phthalate, and chloride ions. It will be shown later in this paper that the same value of a_i represents the experimental data for different buffer ratios, and therefore within the experimental accuracy $a_i=a_1=a_2=a_3$ in phthalate-chloride mixtures.

[8] Harned and Ehlers in their paper used γ for the activity coefficient of hydrochloric acid. The symbol f used in this paper refers to the same numerical values as they give in their paper. It is now the procedure in the National Bureau of Standards to employ the symbol f for activity coefficients on any scale and use the symbols f_c, f_m, and f_x, respectively, for concentrations expressed in moles per liter of solution, moles per 1,000 g of solvent, and in mole fractions.

$$\log (f_H f_{Cl})_{mixture} = -A\sqrt{\mu}/(1+Ba_i\sqrt{\mu}) + 0.133\mu - 0.080\ m_{salt}, \quad (16)$$

and for an ionic strength of 0.5,

$$\log (f_H f_{Cl})_{mixture} = -A\sqrt{\mu}/(1+Ba_i\sqrt{\mu}) + 0.133\mu - 0.0624\ m_{salt}. \quad (17)$$

However, it has been found that the values of $\log (f_H f_{Cl})_{mixture}$ may be represented equally well for both ionic strengths by the single equation

$$\log (f_H f_{Cl})_{mixture} = -A\sqrt{\mu}/(1+Ba_i\sqrt{\mu}) + 0.0635\ m_H + 0.0695 m_{Cl}, \quad (18)$$

with an accuracy of ± 0.0011 in the activity coefficient. Thus, the activity coefficients of hydrochloric acid in acid-salt mixtures may be calculated for different ionic strengths by an equation in which the terms involving β for H^+ and Cl^- ions are considered to be additive. In this treatment the value of a_i for acid-salt mixtures is about the same as for pure hydrochloric acid. Harned and Ehlers [19] obtained a value of 4.3 A. In all buffer mixtures studied by the method in which hydrogen and silver–silver-chloride electrodes are used, a_i should therefore have a value very close to that of hydrochloric acid or 4.3. The value of 3.76 A found in this investigation is considered to be a close approximation. As the addition of potassium salts lowers the activity coefficients of hydrochloric acid, the value of a_i for such mixtures could be somewhat lower than 4.3 A, and the value of 3.76 A obtained here is in accord with this fact.

2. COMPLETE METHOD

In the foregoing it was assumed that the buffer ratio, m_1/m_2, may be determined from the stoichiometrical molalities of acid potassium phthalate and dipotassium phthalate. However, owing to various ionic equilibria this is not strictly true and corrections must therefore be made accordingly.

In a mixture of *o*-phthalic acid with its acid salt, or a mixture of the latter with the completely neutralized salt, the essential equilibria are

$$H_2Ph = H^+ + HPh^-, \quad (19)$$

$$HPh^- = H^+ + Ph^=, \quad (20)$$

which upon subtraction give

$$2HPh^- = H_2Ph + Ph^=, \quad (21)$$

In each case, the ions and molecules are in dynamic equilibrium defined by the mass-action expressions. These give, respectively, for processes 19 and 21

$$K_1 = (a_H f_{HPh} m_{HPh})/(f_{H_2Ph} m_{H_2Ph}), \quad (22)$$

and

$$K_2/K_1 = (a_{Ph} a_{H_2Ph})/a^2_{HPh} = (f_{Ph} f_{H_2Ph} m_{Ph} m_{H_2Ph})/(f_{HPh} m_{HPh})^2, \quad (23)$$

where the terms have the same significance as above. The expression for process 20 is given by eq 3.

As a result of these equilibria, in a solution composed of KHPh of molality of m_1 and of K_2Ph of a molality of m_2

$$m_{HPh}=m_1-m_H-2m_{H_2Ph}, \tag{24}$$

as HPh^- is removed in process 20 to form H^+ ions and in process 21 to form H_2Ph. Also

$$m_{Ph}=m_2+m_H+m_{H_2Ph}, \tag{25}$$

as HPh^- is removed in process 20 in an amount equivalent to H^+ ions and in process 21 in an amount equivalent to H_2Ph. Consequently, the stoichiometrical molalities of KHPh and K_2Ph will be altered and a quantity of H_2Ph formed as a result of the above processes. However, if K_2/K_1 is less than about 10^{-3}, the tendency of reaction 21 to take place from left to right will be small and m_{H_2Ph} can be neglected in eq 24 and 25, leaving only the corrections for m_H. This was shown in a previous paper to be true for malonic acid for which K_2/K_1 is about 1.4×10^{-3} [8]. The values for m_H are obtained from the emf by eq 13 given above. This entails the method of successive approximations as $\mu=m_1+3m_2+m_3+2m_H$[9]. A preliminary value of m_H is first obtained from the emf, by the use of the stoichiometrical ionic strength. This value of m_H is then used to calculate a new ionic strength, and the process is repeated until self-consistent values of μ and m_H are obtained. Hence two equations, eq 13 and the equation $\mu=m_1+3m_2+m_3+2m_H$ are used in the method of successive approximations.

From data reported in the literature [20] for *o*-phthalic acid, K_2/K_1 is about 3×10^{-3} which exceeds the condition postulated for the neglect of m_{H_2Ph} in eq 24 and 25. Therefore corrections for H_2Ph, sometimes called "overlapping" corrections because H_2Ph and HPh^- are titrated simultaneously, become necessary even though they are small. They may be obtained as follows. If a equals the molality of the acid and b the molality of added alkali, then for any mixture of the two

$$a=m_{H_2Ph}+m_{HPh}+m_{Ph}, \tag{26}$$

and for electrical neutrality

$$b+m_H=m_{HPh}+2\,m_{Ph}. \tag{27}$$

By means of these equations and eq 3 and 22

$$m_{H_2Ph}=[2\,am_H-m_H(b+m_H)]/[2\,m_H+(K_1f_{H2Ph})/(f_Hf_{HPh})], \tag{28}$$

with the condition [10] that eq 29,

$$m_H^3+[a+(K_1f_{H_2Ph})/(f_Hf_{HPh})]m_H^2+[(K_1K_2f_{H_2Ph})/(f_Hf_{Ph})+(bK_1f_{H_2Ph})/(f_Hf_{HPh})-(aK_1f_{H_2Ph})/(f_Hf_{HPh})]\,m_H+$$

$$[(K_1K_2f_{H_2Ph})/(f_H^2f_{Ph})](b-2a)=0, \tag{29}$$

[9] The ionic strength actually is given by $\mu=m_1+3m_2+m_3+2m_H+m_{H_2Ph}$, where value of m_{H_2Ph} is given by eq 28. As values of m_{H_2Ph} are so small, the term m_{H_2Ph} may be neglected in determining the ionic strength.

[10] This condition must be imposed. In the four eq 3, 22, 26 and 27 there are 5 unknowns, namely K_1, K_2, m_{H_2Ph}, m_{HPh}, and m_{Ph}, provided m_H is determined experimentally. Hence an unequivocal solution is not possible without the introduction of a restriction or condition. Frequently, a solution of the equations is obtained in titration experiments by selecting 2 widely separated values for m_H on the titration curve and substituting them in eq 29 and solving the two equations simultaneously for K_1 and K_2. This procedure is the same as imposing a condition.

obtained by the elimination of m_{H_2Ph}, m_{HPh}, and m_{Ph} in eq 3, 22, 26, and 27 is satisfied for the solutions of any composition and concentration. However, solution of eq 28 required a knowledge of m_H, the activity coefficients, K_1, and K_2. Values of m_H can be obtained from the emf by eq 13 described above. Values of K_2 used first are those obtained by the simplified method described above. A value of 1.3×10^{-3} was used for K_1[20].[11] The Debye-Hückel equations were employed to calculate the activity coefficients of the ions and the activity coefficient of H_2Ph was taken equal to unity, as is customary. After values of m_{H_2Ph} are calculated by use of eq 28 they are used in eq 24 and 25 to calculate new values of the molality for the HPh^- and $Ph^=$ ions. These latter values are then used to calculate new values of K_2 and this arithmetical procedure is repeated until self-consistent values of K_2 and m_{H_2Ph} are obtained.

The corrections for both m_H and m_{H_2Ph} become less significant as the ionic strength of the solutions increases. It was found that the total corrections, Δ, may be expressed as a function of the ionic strength by the eq

$$\Delta=(\omega+\lambda\sqrt{\mu})/\mu, \tag{30}$$

where ω and λ are constants independent of the temperature. With these corrections eq 10, 11, and 12 become

$$(E-E^\circ)/(2.3026RT/F)+\log\,(m_3m_1/m_2)-(\omega+\lambda\sqrt{\mu})/\mu+2A\sqrt{\mu}/(1+Ba_i\sqrt{\mu})+\beta\mu=pK_2, \tag{31}$$

$$(E-E^\circ)/(2.3026RT/F)+\log m_{Cl}-A\sqrt{\mu}/(1+Ba_i\sqrt{\mu})-(\omega+\lambda\sqrt{\mu})/\mu+\beta_{Cl}m_{Cl}=pH, \tag{32}$$

and

$$pK_2-\log\,(m_1/m_2)-3A\sqrt{\mu}/(1+Ba_i\sqrt{\mu})+(\omega+\lambda\sqrt{\mu})/\mu+\beta_{Ph}m_{Ph}-\beta_{HPh}m_{HPh}=pH, \tag{33}$$

by which precise values of pH and pK_2 (or K_2) can be computed.

Sometimes the β values are considered to be equal for all the ions involved, or $\beta_1=\beta_2=\beta_3=\beta$. Then eq 33 reduces to

$$pK_2-\log\,(m_1/m_2)-3A\sqrt{\mu}/(1+Ba_i\sqrt{\mu})+(\omega+\lambda\sqrt{\mu})/\mu=pH, \tag{34}$$

containing no β term,[12] and is therefore different from the Henderson-Debye-Hückel equation [21] generally used to express pH as a function of the ionic strength of the solution. In this case, the pH value of the solution could be calculated solely from the values of pK_2 and the concentration of the buffer without regard to salt effects. In eq 34, $-3A\sqrt{\mu}/(1+Ba_i\sqrt{\mu})$ represents the value of $\log(f_{Ph}/f_{HPh})$. However, the logarithm of the ratio of any two activity coefficients does not vary with the ionic strength in accordance solely with the first term of the Debye-Hückel equation. Furthermore, differentiation of eq 34 with respect to μ or $\sqrt{\mu}$ does not give a minimum in the plots of

[11] The calculations are insensitive to the value of K_1. A value of 1.0×10^{-4} or 1.5×10^{-3} will yield substantially the same value of m_{H_2Ph}.

[12] This equation has been shown to be applicable to buffers composed of disodium malonate, acid sodium malonate, and sodium chloride for which β is zero [8]. When β is zero, it is not possible to determine the β values for the individual ions.

(pH vs μ) or (pH vs $\sqrt{\mu}$), a result contrary to observed facts for the pH of several weak buffers [22] and of water in the presence of neutral salts [23]. Eq 34 also requires, for example, that a solution containing 0.1 *M* K_2Ph, 0.1 *M* KHPh, and 0.1 *M* KCl would have the same pH value as one composed of 0.07 *M* K_2Ph, 0.07 *M* KHPh, and 0.22 *M* KCl, or of 0.02 *M* K_2Ph, 0.02 *M* KHPh, and 0.42 *M* KCl, because of the identity in the ionic strength of these three solutions. In short, no "specific salt effects" would be observed and the change in the pH of a solution upon addition of salts could be calculated solely by the theory of Debye and Hückel. It is therefore necessary, in order to explain observed results with phthalates, to use eq 33, which includes the β term.

III. EXPERIMENTAL PROCEDURES

1. MATERIALS AND SOLUTIONS

The solutions used in this investigation were prepared in a CO_2-free atmosphere from known weights of stock solutions containing acid potassium phthalate, dipotassium phthalate, and potassium chloride by dilution with known weights of conductivity water having a specific conductance of 0.6 to 1.0×10^{-6} mho. The stock solutions were prepared by the addition of a calculated amount of dry acid potassium phthalate and dry potassium chloride to a standardized solution of potassium hydroxide, previously freed of carbonate by the addition dropwise of a saturated solution of barium hydroxide until no more precipitate of barium carbonate is formed. The potassium hydroxide solution was prepared from high-grade material, which exceeded the ACS specifications for analytical reagents. It was standardized against benzoic acid, National Bureau of Standards Standard Sample 39 e, in a CO_2-free atmosphere by using phenolphthalein solution as the indicator. Results of five titrations agreed to 0.02 percent. Acid potassium phthalate, NBS Standard Sample 84a, having a certified purity of 100 percent determined by titration, was dried according to the directions given in the Bureau certificate and was allowed to cool in a desiccator containing concentrated sulfuric acid. The potassium chloride was recrystallized twice from conductivity water and then thrice from 95-percent ethanol to remove the last traces of bromide. It was dried for at least 10 hours at 110° C and allowed to cool in a desiccator containing concentrated sulfuric acid. After the solutions were prepared, they were deaerated by hydrogen gas, corrections being made for loss of water from the solutions. All weights were corrected to vacuum. In determining the amount of water lost during the deaeration, corrections were made for the volume of air in the flasks displaced by hydrogen gas by using the density of each gas.

2. ELECTRODES AND APPARATUS

The hydrogen electrodes were platinum foil covered with palladium, according to the directions of Hamer and Acree [2]. Electrodes of this type do not catalyze the reduction of phthalates and they function reversibly for well over 100 hours.

Silver–silver-chloride electrodes of the thermal-electrolytic type were prepared from pure materials by the method described in a previous paper [7]. They were sufficiently aged to bring them to a stable state.

The details of the apparatus employed in these studies, including the cells, bubble tubes, thermostat, and the emf recording instruments have been described by Hamer and Acree [7]. The cells and bubble tubes were filled under reduced pressure, the temperature of the thermostat was controlled within 0.01° C at all the temperatures, and the emf was measured with a calibrated potentiometer and with a galvanometer and a standard cell. The electromotive forces were corrected in the usual manner to 1 atmosphere of hydrogen pressure.

IV. CALCULATION OF THE SECOND DISSOCIATION CONSTANT OF *o*-PHTHALIC ACID

The electromotive forces obtained at 13 temperatures from 0° to 60° C in 4 series of experiments on 4 different buffer ratios, K_2Ph/-KHPh, designated as series A to D, are given in tables 1 to 4 for the different solutions whose compositions are defined in terms of the concentration of acid potassium phthalate given in column 2 and the buffer ratio given at the top of each table. Table 5 gives the electromotive forces recorded for the same temperature range for seven less complete series of measurements on seven other buffer ratios, designated as series E to K. A number of dilutions were made in series A to D, whereas only two dilutions were made in the other seven series. Hence, only the first four series were used for the determination of pK_2 (or K_2) and the last seven together with the first four were used to determine the β values of the various ions of the mixtures. In series A to D the solutions had a buffer ratio, respectively, of 1.0057, 1.5070, 2.0005, and 2.0223; and a chloride-acid phthalate ratio, KCl/KHPh, respectively, of 1.0014, 1.0035, 1.0006, and 0.1858. Measurements of the emf were made for two slightly different ratios (see footnotes of tables 1 and 2). In the other series of experiments, the buffer ratio ranged from approximately 1 to 2, but the chloride-acid phthalate ratio varied considerably from approximately 0.09 to 0.70.

TABLE 1.—*Electromotive forces of galvanic cells with hydrogen and silver–silver-chloride electrodes and containing mixtures of phthalates and chlorides*

[Series A, Molality of dipotassium phthalate=1.0057×molality of acid potassium phthalate. Molality of potassium chloride=1.0014×molality of acid potassium phthalate]

Solution number	Molality of KHPh	Temperature in degrees centigrade					
		0	5	10	15	20	25
	Moles of solute per 1,000 g of water	v	v	v	v	v	v
A1	0.0007661	0.69696	0.70191	0.70723	0.71243	0.71781	0.72333
A2	.0014530	.68072	.68542	.69032	.69526	.70033	.70560
A3	.0016690	.67744	.68200	.68683	.69171	.69665	.70190
A4	.0023505	.66826	.67305	.67771	.68248	.68725	.69223
A5	.0031721	.66054	.66504	.66956	.67411	.67886	.68368
A6	.0034678	.65817	.66256	.66709	.67161	.67624	.68102
A7	.0036275	.65701	.66142	.66594	.67043	.67498	.67980
A8	.0048224	.64961	.65378	.65820	.66244	.66701	.67162
A9	.0049454	.64894	.65326	.65745	.66184	.66635	.67082
A10	.0069349	.63997	.64396	.64814	.65230	.65658	.66100
A11	.0095161	.63147	.63534	.63935	.64335	.64746	.65171
A12	.011319	.62675	.63059	.63451	.63830	.64231	.64664
A13	.014671	.61968	.62327	.62705	.63081	.63474	.63876
A14	.018381	.61345	.61702	.62068	.62432	.62813	.63190
A15	.023770	.60643	.60986	.61341	.61670	.62036	.62416
A16	.026358	.60357	.60688	.61027	.61376	.61731	.62093
A17	.027847	.60212	.60535	.60889	.61213	.61559	.61940
A18	.041527	.59098	.59407	.59718	.60042	.60376	.60705
A19	.062963	.57950	.58223	.58522	.58808	.59118	.59428
A20	.10781	.56477	.56726	.56990	.57244	.57514	.57800
A'1 *	.10803	.56468	.56716	.56979	.57237	.57508	.57789

Solution number	Temperature in degrees centigrade						
	30	35	40	45	50	55	60
	v	v	v	v	v	v	v
A1	0.72886	0.73339	0.74020	0.74595	0.75194	0.75802	0.76444
A2	.71077	.71598	.72148	.72685	.73259	.73836	.74454
A3	.70701	.71216	.71759	.72296	.72851	.73441	.74081
A4	.69725	.70225	.70751	.71271	.71809	.72380	.72934
A5	.68845	.69334	.69845	.70349	.70871	.71429	.71992
A6	.68581	.69063	.69565	.70065	.70589	.71141	.71689
A7	.68456	.68938	.69436	.69934	.70456	.71005	.71556
A8	.67612	.68085	.68575	.69058	.69551	.70099	.70622
A9	.67556	.68016	.68503	.68965	.69467	.70004	.70532
A10	.66543	.66981	.67455	.67918	.68406	.68921	.69437
A11	.65891	.66022	.66469	.66912	.67391	.67876	.68387
A12	.65057	.65478	.65934	.66371	.66825	.67306	.67795
A13	.64278	.64684	.65101	.65530	.65975	.66436	.66923
A14	.63585	.63986	.64390	.64799	.65233	.65693	.66161
A15	.62791	.63165	.63560	.63961	.64366	.64811	.65289
A16	.62468	.62842	.63237	.63614	.64026	.64470	.64917
A17	.62306	.62658	.63057	.63448	.63837	.64287	.64716
A18	.61054	.61395	.61757	.62119	.62509	.62917	.63331
A19	.59745	.60072	.60415	.60732	.61096	.61480	.61965
A20	.58081	.58370	.58672	.58940	.59281	.59633	.59985
A'1 *	.58072	.58358	.58666	.58960	.59282	.59630	.59972

* Molality of dipotassium phthalate=1.0074×molality of acid potassium phthalate. Molality of potassium chloride=1.0037×molality of acid potassium phthalate.

TABLE 2.—*Electromotive forces of galvanic cells with hydrogen and silver–silver-chloride electrodes and containing mixtures of phthalates and chlorides*

[Series B, Molality of dipotassium phthalate = 1.5070 × molality of acid potassium phthalate. Molality of potassium chloride = 1.0035 × molality of acid potassium phthalate]

Solution number	Molality of KHPh	Temperature in degrees centigrade					
		0	5	10	15	20	25
	Moles of solute per 1,000 g of water	v	v	v	v	v	v
B1	0.0004400	0.71979	0.72528	0.73096	0.73663	0.74248	0.74838
B2	.0006264	.71109	.71642	.72200	.72744	.73303	.73886
B3	.0011836	.69480	.69987	.70508	.71028	.71566	.72108
B4	.0018128	.68392	.68884	.69385	.69884	.70401	.70922
B5	.0023519	.67719	.68190	.68676	.69165	.69668	.70176
B6	.0030064	.67085	.67546	.68022	.68495	.68986	.69482
B7	.0034327	.66730	.67190	.67653	.68120	.68600	.69093
B8	.0035250	.66654	.67113	.67581	.68046	.68530	.69018
B9	.0048817	.65808	.66242	.66687	.67136	.67603	.68073
B10	.0069713	.64850	.65263	.65694	.66125	.66573	.67023
B11	.0087820	.64227	.64643	.65042	.65459	.65895	.66334
B12	.0088235	.64201	.64616	.65025	.65443	.65878	.66317
B13	.0069534	.64166	.64572	.64991	.65408	.65842	.66284
B14	.013470	.63057	.63445	.63832	.64236	.64644	.65054
B15	.017045	.62417	.62782	.63166	.63547	.63946	.64348
B16	.034937	.60433	.60767	.61093	.61445	.61802	.62163
B17	.051843	.59353	.59662	.59974	.60292	.60628	.60962
B18	.071943	.58472	.58761	.59060	.59355	.59671	.59986
B'1 [a]	.071886	.58473	.58761	.59068	.59360	.59668	.59988

Solution number	Temperature in degrees centigrade						
	30	35	40	45	50	55	60
	v	v	v	v	v	v	v
B1	0.75433	0.76034	0.76651	0.77269	0.77910	0.78576	0.79240
B2	.74464	.75049	.75649	.76250	.76874	.77523	.78149
B3	.72656	.73210	.73779	.74349	.74942	.75560	.76175
B4	.71449	.71981	.72530	.73078	.73650	.74246	.74834
B5	.70690	.71209	.71745	.72280	.72839	.73421	.74001
B6	.69984	.70490	.71013	.71535	.72082	.72651	.73219
B7	.69587	.70087	.70603	.71120	.71659	.72222	.72782
B8	.69511	.70009	.70523	.71038	.71575	.72137	.72696
B9	.68549	.69031	.69528	.70025	.70546	.71089	.71631
B10	.67482	.67945	.68422	.68900	.69401	.69926	.70461
B11	.66785	.67240	.67694	.68159	.68648	.69168	.69668
B12	.66761	.67211	.67676	.68141	.68629	.69150	.69659
B13	.66724	.67173	.67637	.68101	.68589	.69109	.69617
B14	.65475	.65901	.66342	.66784	.67248	.67735	.68226
B15	.64756	.65168	.65596	.66025	.66474	.66948	.67403
B16	.62524	.62896	.63286	.63674	.64079	.64511	.64936
B17	.61304	.61650	.62011	.62372	.62755	.63163	.63561
B18	.60307	.60632	.60972	.61312	.61673	.62058	.62427
B'1 [a]	.60309	.60636	.60975	.61316	.61678	.62065	.62450

[a] Molality of dipotassium phthalate = 1.5139 × molality of acid potassium phthalate. Molality of potassium chloride = 1.0056 × molality of acid potassium phthalate.

TABLE 3.—*Electromotive forces of galvanic cells with hydrogen and silver–silver-chloride electrodes and containing mixtures of phthalates and chlorides*

[Series C, Molality of dipotassium phthalate=2.0005×molality of acid potassium phthalate. Molality of potassium chloride=1.0006×molality of acid potassium phthalate]

Solution number	Molality of KHPh	Temperature in degrees centigrade					
		0	5	10	15	20	25
	Moles of solute per 1,000 g of water	v	v	v	v	v	v
C1	0.0012203	0.70038	0.70554	0.71085	0.71616	0.72158	0.72715
C2	.0025363	.68043	.68518	.69008	.69504	.70003	.70531
C3	.0044644	.66459	.67098	.67565	.68023	.68508	.68997
C4	.0067742	.64833	.65250	.65671	.66106	.66544	.67002
C5	.010675	.64287	.64096	.65125	.65543	.65960	.66411
C6	.016461	.63111	.63491	.63880	.64273	.64685	.65104
C7	.022447	.62254	.62621	.63000	.63377	.63773	.64139
C8	.030548	.61408	.61755	.62113	.62485	.62844	.63235
C9	.036014	.60964	.61296	.61645	.61993	.62350	.62724
C10	.042177	.60532	.60855	.61202	.61549	.61896	.62263
C11	.054400	.59848	.60161	.60488	.60811	.61147	.61491

Solution number	Temperature in degrees centigrade						
	30	35	40	45	50	55	60
	v	v	v	v	v	v	v
C1	0.73273	0.73835	0.74414	0.74993	0.75595	0.76228	0.76854
C2	.71059	.71578	.72110	.72656	.73216	.73813	.74395
C3	.69502	.69988	.70504	.71008	.71537	.72112	.72666
C4	.67458	.67924	.68383	.68860	.69365	.69895	.70413
C5	.66851	.67305	.67768	.68221	.68716	.69232	.69744
C6	.65535	.65944	.66393	.66826	.67290	.67777	.68256
C7	.64561	.64983	.65389	.65811	.66267	.66747	.67189
C8	.63612	.63994	.64399	.64800	.65223	.65681	.66125
C9	.63104	.63481	.63870	.64267	.64698	.65122	.65559
C10	.62614	.62995	.63363	.63756	.64158	.64604	.65007
C11	.61838	.62200	.62557	.62926	.63334	.63716	.64142

TABLE 4.—*Electromotive forces of galvanic cells with hydrogen and silver–silver-chloride electrodes and containing mixtures of phthalates and chlorides*

[Series D, Molality of dipotassium phthalate=2.0223×molality of acid potassium phthalate. Molality of potassium chloride=0.1858×molality of acid potassium phthalate]

Solution number	Molality of KHPh	Temperature in degrees centigrade					
		0	5	10	15	20	25
	Moles of solute per 1,000 g of water	v	v	v	v	v	v
D1	0.014013	0.67591	0.68055	0.68537	0.69022	0.69502	0.70002
D2	.023409	.66180	.66620	.67070	.67522	.67986	.68454
D3	.024878	.66019	.66450	.66895	.67341	.67796	.68279
D4	.030089	.65416	.65840	.66273	.66697	.67149	.67606
D5	.042383	.64569	.64978	.65395	.65815	.66234	.66672
D6	.043083	.64531	.64934	.65358	.65772	.66189	.66634
D7	.053814	.63940	.64335	.64741	.65128	.65548	.65965

TABLE 4.—*Electomotive forces of galvanic cells with hydrogen and silver–silver-chloride electrodes and containing mixture of phthalates and chlorides*—Con.

Solution number	Temperature in degrees centigrade						
	30	35	40	45	50	55	60
	E	E	E	E	E	E	E
D1	0.70445	0.71011	0.71535	0.72054	0.72006	0.73190	0.73754
D2	.68927	.69397	.69892	.70396	.70905	.71454	.71987
D3	.68743	.69221	.69711	.70194	.70690	.71264	.71784
D4	.68062	.68516	.68980	.69481	.69969	.70506	.71020
D5	.67110	.67558	.68012	.68470	.68953	.69467	.69958
D6	.67068	.67510	.67965	.68425	.68897	.69411	.69906
D7	.66388	.66818	.67255	.67510	.68168	.68665	.69145

TABLE 5.—*Electromotive forces of galvanic cells with hydrogen and silver–silver-chloride electrodes and containing mixtures of phthalates and chlorides*

Solution number	Molality of KHPh	Molality of K_2Ph / Molality of KHPh	Molality of KCl / Molality of KHPh	Temperature in degrees centigrade				
				0	5	10	15	20
	Moles of solute per 1,000 g of water			E	E	E	E	E
E1	0.055730	1.0074	0.6479	0.60356	0.59672	0.59069	0.60312	0.60044
E2	.10803	1.0074	.6479	.57556	.57831	.58109	.58388	.58678
F1	.053194	1.0074	.2777	.61530	.61879	.62243	.62610	.62980
F2	.10803	1.0074	.2777	.59613	.59920	.60242	.60561	.60891
G1	.075592	1.0074	.09257	.63196	.63563	.63959	.64237	.64742
G2	.10803	1.0074	.09257	.62230	.62590	.62957	.63325	.63705
H1	.036174	1.5139	.6956	.61234	.61586	.61946	.62304	.62660
H2	.071886	1.5139	.6956	.59378	.59685	.60006	.60321	.60641
I1	.024728	1.5139	.4143	.63525	.63917	.64380	.64724	.65184
I2	.071886	1.5139	.4143	.59620	.60054	.61296	.61636	.61990
J1	.054840	1.5139	.1392	.63952	.64349	.64757	.65143	.65569
J2	.071886	1.5139	.1392	.63219	.63604	.63997	.64383	.64776
K1	.026688	2.0223	.5575	.63214	.63595	.63992	.64388	.64790
K2	.053814	2.0223	.5575	.61319	.61661	.62014	.62371	.62731

Solution number	Temperature in degrees centigrade							
	25	30	35	40	45	50	55	60
	E	E	E	E	E	E	E	E
E1	0.60987	0.61329	0.61683	0.62047	0.62408	0.62795	0.63207	0.63617
E2	.58982	.59284	.59592	.59914	.60231	.60587	.60950	.61313
F1	.63360	.63747	.64144	.64544	.64940	.65375	.65831	.66285
F2	.61230	.61574	.61918	.62288	.62643	.63025	.63434	.63840
G1	.65153	.65565	.65990	.66422	.66849	.67306	.67784	.68259
G2	.64197	.64489	.64882	.65288	.65697	.66132	.66587	.67039
H1	.63048	.63428	.63813	.64218	.64614	.65037	.65491	.66031
H2	.60979	.61319	.61662	.62021	.62377	.62751	.63098	.63556
I1	.65561	.65986	.66419	.66870	.67311	.67780	.68279	.68775
I2	.62350	.62713	.63086	.63462	.63846	.64258	.64680	.65110
J1	.65995	.66422	.66854	.67305	.67748	.68222	.68716	.69204
J2	.65196	.65604	.66020	.66450	.66888	.67343	.67818	.68291
K1	.65202	.65619	.66050	.66484	.66918	.67379	.67866	.68345
K2	.63103	.63478	.63863	.64255	.64652	.65062	.65501	.66006

The emf was used in eq 9 and 31 to calculate pK'_2 by the use of data for E° determined by Harned and Ehlers [19] and values of R, T, and F given by Hamer, Burton and Acree [8]. It was found that a_i must be assigned a value of 3.76 ± 0.07A at all the temperatures in order for pK'_2 to vary linearly with the ionic strength. In figure 1, values of pK'_2 for the more dilute solutions are shown plotted against the ionic strength for series A to C at 25° C. The dotted line corresponds to the values of pK'_2 calculated on the basis of stoichiometrical molalities alone (eq 9), and the solid line to values corrected for the various processes depicted above, that is, for the

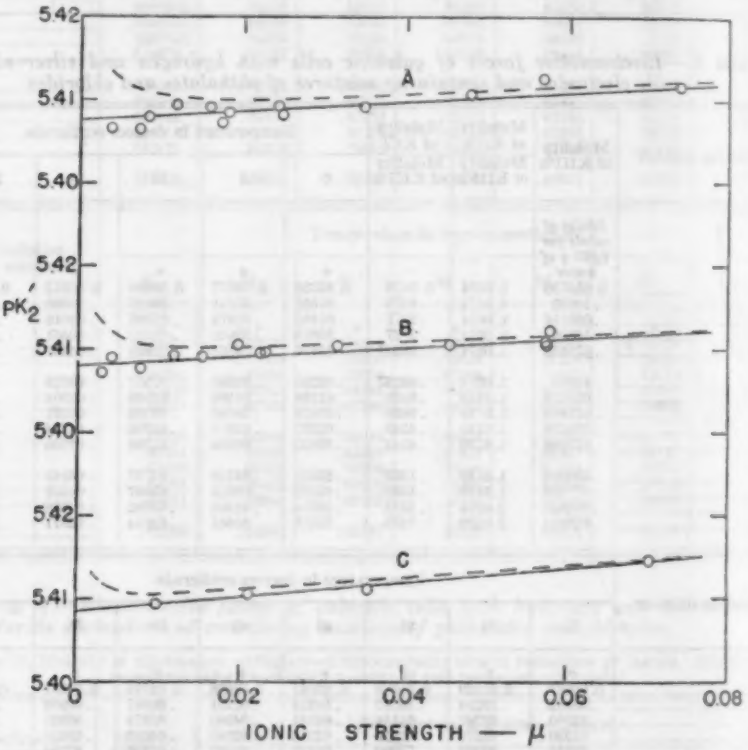

FIGURE 1.—*Plots of pK'_2 as a function of the ionic strength for dilute solutions of phthalate-chloride mixtures.*

Dotted line corresponds to stoichiometrical molalities. Solid line corresponds to ionic molalities. A, B, and C refer to the series of experiments designated by the same letters.

hydrogen-ion and *o*-phthalic acid (or overlapping) corrections (eq 30). These corrections become less as the buffer ratio becomes larger, or the higher the pH of the solution is from that corresponding to the first equivalence point, as is indicated in the graph. These corrections vary with the ionic strength, becoming less as the ionic strength increases, and may be computed for the 13 temperatures by eq 30 given above. Numerical values of these constants are given in table 6 for the various buffer and chloride ratios. In figure 2, values of pK'_2, calculated by eq 31 with a value of 3.76 A for a_i, are shown

plotted against the ionic strength for series A to D at temperatures of 0°, 25°, 45°, and 60° C. Plots for the other temperatures are similar. The slopes of the lines give the magnitudes of the constant—β of eq 31, and the extrapolated value at zero ionic strength gives the value of pK_2, free of disturbing effects of the salts, the medium, or ionic association. Any value of a_i, different from 3.76 A, would give a curved line; neglect of the last term on the left side of eq 31 would give much lower values of pK'_2, which when plotted against the ionic strength would give a very marked curvature, concave to

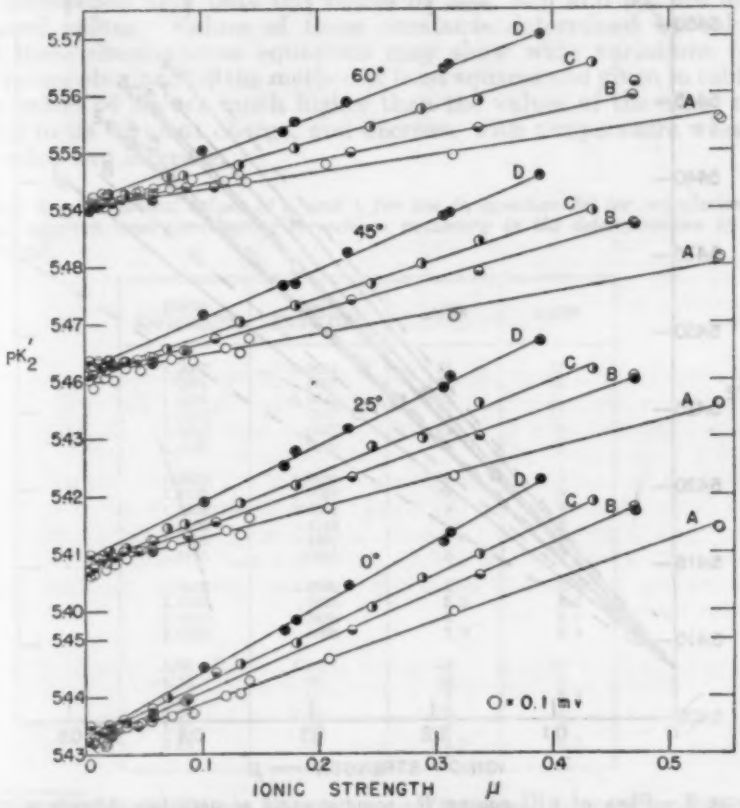

FIGURE 2.—*Extrapolation plots of* pK'_2 *against the ionic strength.*
A, B, C, and D refer to the series of experiments designated by the same letters.

the axis of the abscissa; and the use of a value of zero for a_i (Debye-Hückel limiting law) would give much higher values of pK'_2, which when plotted against the ionic strength would give a curve convex to the axis of the abscissa.[13] In figure 3, values of pK'_2, calculated by eq 31 with an a_i value of 3.76 A, are shown plotted as ordinates against the ionic strength as abscissas for the other buffer and chloride ratios at 25° C. Graphs for the other temperatures are similar to these plots. The negative of the slopes of the lines again gives the

[13] See references [7, 8, and 24] for more details concerning the proper choice of values for a_i.

magnitude of the constant β of eq 31. Numerical values of β are given in table 7 for the different temperatures and various buffer and chloride ratios. The β values are a function of the buffer and chloride ratios, being higher for larger buffer ratios and lower chloride ratios. The β values in all cases decrease with respect to temperature. The data given in the table are smooth values, which were read from a large-scale plot of β against temperature and buffer and chloride ratios and are accurate on the average to 0.004 unit. It

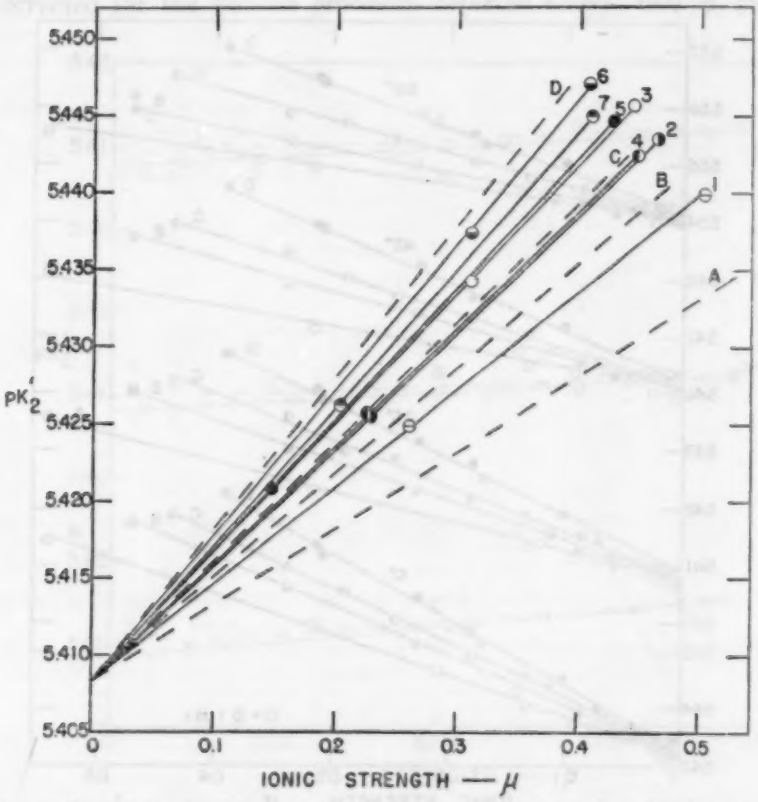

FIGURE 3.—*Plots of* pK'_2 *against the ionic strength of phthalate-chloride mixtures, for a temperature of 25° C.*

Dotted lines correspond to values of pK'_2 for series A, B, C, and D shown plotted in figure 2.

1, $K_2Ph=1.0074\times KHPh$ and $KCl=0.6479\times KHPh$ (series E)
2, $K_2Ph=1.0074\times KHPh$ and $KCl=0.2777\times KHPh$ (series F)
3, $K_2Ph=1.0074\times KHPh$ and $KCl=0.09257\times KHPh$ (series G)
4, $K^3Ph=1.5139\times KHPh$ and $KCl=0.6956\times KHPh$ (series H)
5, $K^3Ph=1.5139\times KHPh$ and $KCl=0.4143\times KHPh$ (series I)
6, $K^3Ph=1.5139\times KHPh$ and $KCl=0.1392\times KHPh$ (series J)
7, $K^3Ph=2.0223\times KHPh$ and $KCl=0.5575\times KHPh$ (series K)

may be assumed that the values of β are independent of the ionic species in the solutions or that they apply to each ion, which would then concentrate all the effects of the salts, medium, or ionic associations at finite concentrations on the activity coefficient of the hydrogen ion and would lead to eq 34, given above. However, it has

been shown that this equation is inadequate. Therefore, the β values were considered to be dependent upon the kind and amount of the ionic species present in the solutions and to be given by $(-\beta_{Cl}m_{Cl}-\beta_{HPh}m_{HPh}+\beta_{Ph}m_{Ph})/\mu$ for each buffer and chloride ratio. By using the β values for each of the 11 ratios studied in 11 simultaneous equations, β_{Cl}, β_{HPh}, and β_{Ph} were evaluated by the method of least squares for each of the 13 temperatures.[14] The values are given in the last three rows of table 7. These values make possible the calculation of the values of pK_2' and pH for any buffer ratio between 1 and 2 and for any chloride ratio from 0 to 1. It should be emphasized here that the values of β_{HPh}, β_{Cl}, and β_{Ph} are least-squared values. Values of these constants determined by solving any three simultaneous equations may show wide variations from the values obtained by the method of least squares and given in table 7. The values of β_{Ph} are much higher than the values of the other two, owing to its bivalent charge, and decrease with temperature whereas the other two increase.

TABLE 6.—*Numerical values of* ω *and* λ *for use in equation 30 for calculations of hydrogen-ion and overlapping corrections necessary in the determination of* pK_2 *and* pH

Ratio $K_2Ph/KHPh$	Ratio KCl/KHPh	$\omega\times10^4$	$\lambda\times10^4$
1.0057	1.0014	15	11
1.0074	1.0037	15	11
1.0074	0.6480	14	11
1.0074	.2777	12	11
1.0074	.09257	12	11
1.0074	.0000	11	11
1.5070	1.0035	10	9
1.5139	1.0056	10	9
1.5139	0.6935	9	9
1.5139	.4143	8	9
1.5139	.1392	7	9
1.5139	.0000	6	9
2.0005	1.0006	5	8.5
2.0223	.5575	3.5	8.5
2.0223	.1858	2	8.5
2.0223	.0000	1.2	8.5
1.00	1.00	15	11
1.50	1.00	10	9
2.00	1.00	5	8.5
1.00	0.00	11	11
1.50	.00	6	9
2.00	.00	1.2	8.5

[14] See Kilpatrick [25] and Hitchcock [26] for a discussion of this subject. See also Morton [27] for a discussion of salt effects and Scatchard [15] for a treatment of concentrated solutions.

TABLE 7.—*Numerical values of the constant β in the Debye-Hückel equation for activity coefficients for various mixtures of acid potassium phthalate, dipotassium phthalate, and potassium chloride*

Series number	Temperature in degrees centigrade												
	0	5	10	15	20	25	30	35	40	45	50	55	60
A	−0.068	−0.064	−0.061	−0.057	−0.054	−0.050	−0.047	−0.044	−0.040	−0.037	−0.033	−0.030	−0.028
B	−.085	−.082	−.078	−.075	−.071	−.068	−.064	−.061	−.057	−.054	−.050	−.047	−.044
C	−.096	−.092	−.089	−.085	−.082	−.078	−.075	−.072	−.068	−.065	−.061	−.058	−.054
D	−.116	−.113	−.110	−.106	−.103	−.099	−.096	−.092	−.089	−.085	−.082	−.077	−.075
E	−.080	−.076	−.073	−.069	−.065	−.062	−.059	−.055	−.052	−.048	−.045	−.041	−.038
F	−.094	−.090	−.087	−.083	−.080	−.076	−.073	−.070	−.066	−.063	−.059	−.056	−.052
G	−.102	−.098	−.095	−.091	−.088	−.084	−.081	−.078	−.074	−.071	−.067	−.064	−.060
H	−.093	−.089	−.087	−.083	−.080	−.076	−.073	−.070	−.066	−.063	−.060	−.057	−.053
I	−.100	−.097	−.094	−.090	−.088	−.085	−.082	−.079	−.076	−.073	−.070	−.067	−.064
J	−.109	−.106	−.103	−.100	−.097	−.094	−.091	−.088	−.085	−.082	−.079	−.075	−.072
K	−.107	−.103	−.100	−.096	−.093	−.089	−.082	−.082	−.079	−.075	−.072	−.068	−.065
Ionic species [a]													
$Ph^=$	−.42	−.41	−.41	−.40	−.39	−.38	−.37	−.36	−.35	−.34	−.33	−.32	−.31
HPh^-	−.002	−.006	−.011	−.015	−.018	−.023	−.026	−.029	−.033	−.036	−.040	−.041	−.048
Cl^-	−.082	−.086	−.090	−.094	−.099	−.10	−.11	−.11	−.12	−.12	−.12	−.13	−.13

[a] $Ph^=$, HPh^-, and Cl^- denote the diphthalate, acid phthalate, and chloride ions, respectively.

Values of pK_2 were then determined for the series of experiments A to D, the corresponding values of β being used. They are shown in figure 4 plotted as a function of the ionic strength. This figure is in reality a deviation plot. The average value of pK_2 with the mean deviation for each series is given in table 8. The average value of the four determinations with the total mean deviation is given in column 6 for each temperature. The deviations range from 0.0004 to 0.0011, which correspond to 0.02 to 0.07 mv in the emf. Values of the second dissociation constant of *o*-phthalic acid are given in the last column of this table.

TABLE 8.—*Summary of numerical values of* pK_2 *and* K_2 *calculated from measurements of four different buffer ratios at temperatures of 0° to 60° C*

Temperature	pK_2					$K_2 \times 10^3$
	Series A	Series B	Series C	Series D	Average	Average
°C						
0	[a]5.4319 ±0.0007	5.4326 ±0.0008	5.4324 ±0.0005	5.4323 ±0.0008	5.4323 ±0.0007	3.696
5	5.4177 ± .0010	5.4182 ± .0007	5.4178 ± .0004	5.4184 ± .0006	5.4180 ± .0008	3.820
10	5.4091 ± .0009	5.4093 ± .0008	5.4095 ± .0005	5.4103 ± .0008	5.4096 ± .0009	3.894
15	5.4043 ± .0008	5.4050 ± .0007	5.4053 ± .0008	5.4060 ± .0012	5.4052 ± .0009	3.934
20	5.4041 ± .0009	5.4051 ± .0008	5.4047 ± .0006	5.4053 ± .0006	5.4048 ± .0008	3.937
25	5.4077 ± .0008	5.4079 ± .0007	5.4085 ±.0006	5.4090 ± .0010	5.4083 ± .0008	3.906
30	5.4150 ± .0008	5.4154 ± .0007	5.4165 ±.0011	5.4160 ± .0006	5.4157 ± .0009	3.848
35	5.4259 ± .0010	5.4269 ± .0008	5.4278 ±.0008	5.4276 ± .0007	5.4271 ± .0010	3.740
40	5.5522 ± .0009	5.4423 ± .0007	5.4426 ±.0007	5.4423 ± .0009	5.4424 ± .0008	3.611
45	5.4613 ± .0010	5.4615 ± .0006	5.4616 ±.0006	5.4625 ± .0005	5.4617 ± .0008	3.454
50	5.4846 ± .0008	5.4848 ± .0007	5.4857 ±.0011	5.4849 ± .0005	5.4849 ± .0009	3.274
55	5.5108 ± .0011	5.5116 ± .0006	5.5128 ±.0008	5.5137 ± .0007	5.5122 ± .0011	3.075
60	5.5416 ± .0009	5.5403 ± .0005	5.5414 ±.0005	5.5418 ± .0007	5.5413 ± .0009	2.875

[a] Arithmetical mean deviations.

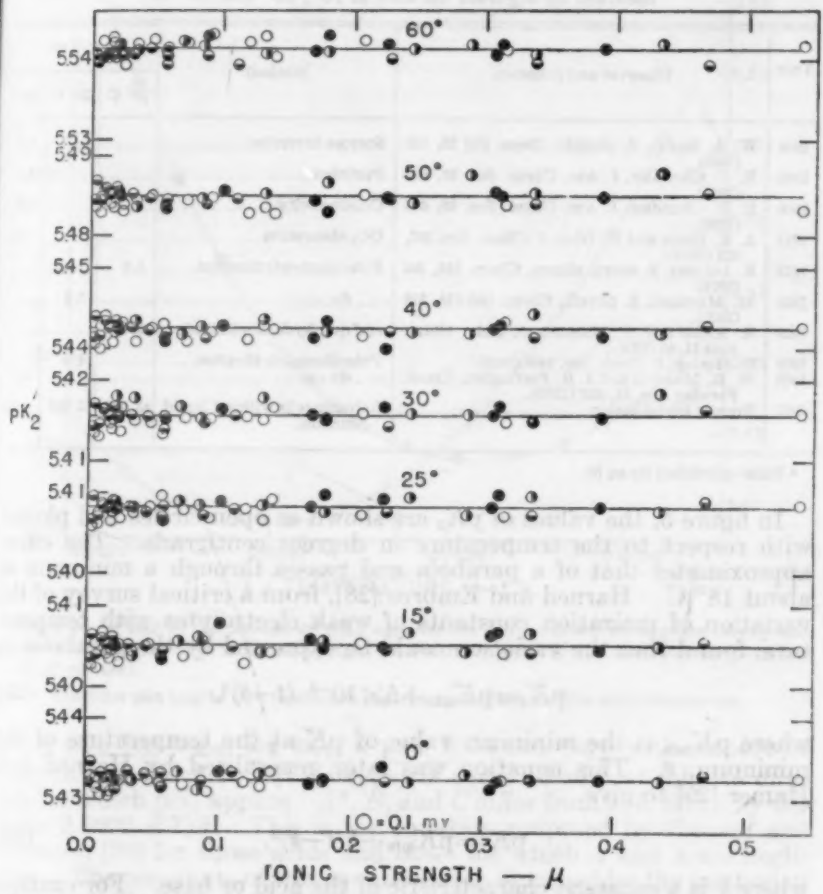

FIGURE 4.—*Plots of all values of* pK'_2 *for series A, B, C, and D at* 0°, 15°, 25°, 30°, 40°, 50°, and 60° *C as a function of the ionic strength.*

This plot represents a deviation plot.

(The symbols represent the same series of experiments given in figure 2.)

In table 9, the values of K_2 are compared with those obtained by other investigators at 18°, 20°, and 25° C. A critical comparison is not possible as previous investigations were limited to a single temperature and involved a number of uncertainties.

TABLE 9.—*Numerical values of the second ionization constant of orthophthalic acid obtained by different workers at 18°, 20° and 25° C*

Year	Observer and reference	Method	$K_2 \times 10^6$		
			18° C	20° C	25° C
1898	W. A. Smith, Z. physik. Chem. [B] **25**, 193 (1898).	Sucrose inversion			1.7
1908	E. E. Chandler, J. Am. Chem. Soc. **30**, 694 (1908).	Partition			3.1
1908	E. E. Chandler, J. Am. Chem. Soc. **30**, 694 (1908).	Conductivity			3.9
1915	A. K. Datta and N. Dhar, J. Chem. Soc. **107**, 824 (1915).	CO_2 absorption			1.82
1924	E. Larsson, Z. anorg. allgem. Chem. **140**, 292 (1924).	Potentiometric titration	4.0		
1925	M. Mizutani, Z. physik. Chem. [B] **118**, 318 (1925).	do		5.8	
1928	R. Kuhn and A. Wasserman, Helv. Chim. Acta **11**, 44 (1928).	emf quinhydrone electrode	3.9		
1928	C. Morton, J. Chem. Soc. 1406 (1928)	Potentiometric titration		4.6	
1935	W. R. Maxwell and J. R. Partington, Trans. Faraday Soc. **31**, 922 (1935).	do			5.2
1945	Present investigation	Galvanic cells without liquid junction.	[a]3.936	3.937	3.936

[a] Value calculated by eq 38.

In figure 5, the values of pK_2 are shown as open circles and plotted with respect to the temperature in degrees centigrade. The curve approximates that of a parabola and passes through a minimum at about 18° C. Harned and Embree [28], from a critical survey of the variation of ionization constants of weak electrolytes with temperature, found that the variation could be expressed by the parabolic eq

$$pK_t = pK_{min} + 5 \times 10^{-5} \ (t-\theta)^2, \tag{35}$$

where pK_{min} is the minimum value of pK at the temperature of the minimum, θ. This equation was later generalized by Harned and Hamer [29] to give

$$pK_t = pK_{min} + k(t-\theta)^2, \tag{36}$$

where k is a constant characteristic of the acid or base. For example k is 8×10^{-5} for the bisulfate ion [16] and 6.4×10^{-5} for the bimalonate ion [8]. It was found that eq 35 only approximately reproduces the experimental values, the mean deviation being 0.014, which greatly exceeds the experimental error. Equation 36, with $pK_{min} = 5.4049$, $k = 8 \times 10^{-5}$, and $\theta = 18.5$, reproduces the experimental data very well except at 60° C, where a deviation of 0.0014 is found. An equation expressing the relation between pK_2 and the temperature may be obtained from eq 31. Both the emf obtained in this investigation and E° obtained by Harned and Ehlers vary quadratically with the temperature, and can be expressed by an equation of the form, $(E - E^\circ = a + bt + ct^2)$. Therefore,

$$pK_2 = A^*/T + B + CT, \tag{37}$$

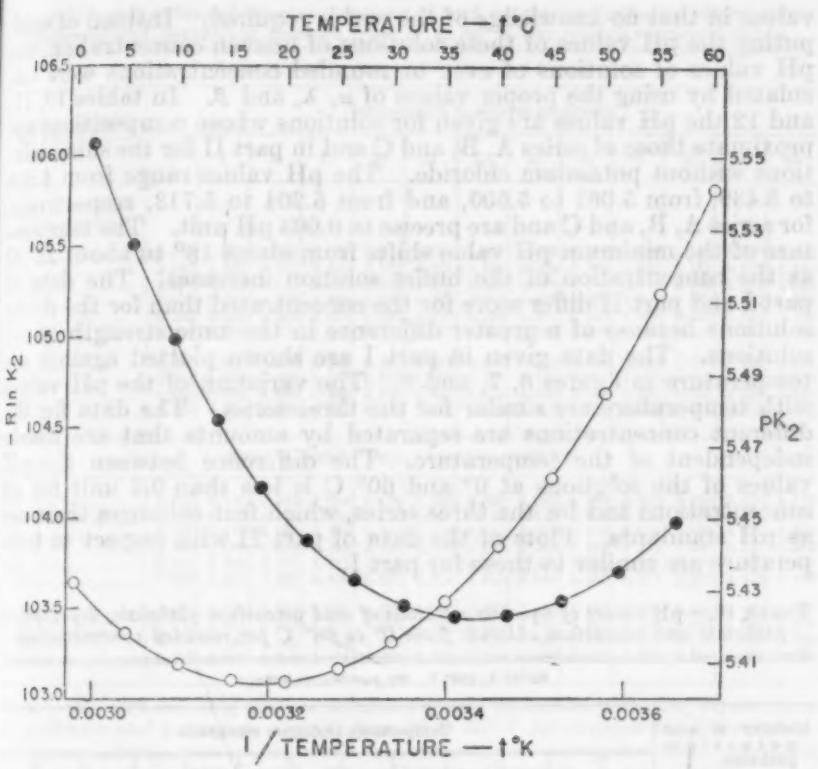

FIGURE 5.—*Plots of the values of* pK_2 *against the temperature in degrees centigrade (open circles) and of* $-R \ln K_2$ *against the reciprocal of the absolute temperature (dark circles).*

The latter plot may be used to evaluate the heat of dissociation of the acid-phthalate ion.

as log m_{Cl}, log m_{HPh}, log m_{Ph}, ω and λ do not vary with respect to temperature and $2A\sqrt{\mu}/(1+Ba_i\sqrt{\mu})$ is equal to zero at infinite dilution for which pK_2 applies. A^*, B, and C differ from a, b, and c by the factor 2.3026 RT/F. This is the equation proposed by Harned and Robinson [30] for those acids and bases for which ω and λ are negligible. The constants of this equation were obtained by the method of least squares and the use of the average values of pK_2 given in table 8. The values of pK_2 are given with a mean deviation of 0.0008 by the equation

$$pK_2 = 2175.83/T - 9.55075 + 0.025694T, \qquad (38)$$

where $T = t\ °C + 273.16$.

V. pH VALUES OF PHTHALATE-CHLORIDE SOLUTIONS

The pH value of each solution of the four main series of experiments and of the seven less complete series used in the evaluation of K_2 may be computed either by eq 32 or 33 by using 3.76 A for a_i, the values of ω and λ given in table 6 and the values of β given in table 7. For synthetic solutions, eq 33 is preferable for the calculation of the pH

values in that no knowledge of the emf is required. Instead of computing the pH values of these solutions of uneven concentration, the pH values of solutions of even or rounded concentrations were calculated by using the proper values of ω, λ, and β. In tables 10, 11, and 12 the pH values are given for solutions whose compositions approximate those of series A, B, and C and in part II for the same solutions without potassium chloride. The pH values range from 4.868 to 5.439, from 5.061 to 5.600, and from 5.204 to 5.713, respectively, for series A, B, and C and are precise to 0.003 pH unit. The temperature of the minimum pH value shifts from about 18° to about 25° C as the concentration of the buffer solution increases. The data of part I and part II differ more for the concentrated than for the dilute solutions because of a greater difference in the ionic strength of the solutions. The data given in part I are shown plotted against the temperature in figures 6, 7, and 8. The variation of the pH values with temperature are similar for the three series. The data for the different concentrations are separated by amounts that are nearly independent of the temperature. The difference between the pH values of the solutions at 0° and 60° C is less than 0.1 unit for all concentrations and for the three series, which fact enhances their use as pH standards. Plots of the data of part II with respect to temperature are similar to those for part I.

TABLE 10.—pH *values of aqueous solutions of acid potassium phthalate, dipotassium phthalate and potassium chloride from 0° to 60° C for rounded concentrations*

Series A, part 1. $m_{K_2Ph}=m_{KHPh}=m_{KCl}$

Molality of acid potassium phthalate	Temperature in degrees centigrade												
	0	5	10	15	20	25	30	35	40	45	50	55	60
Moles of solute/1,000 g of water													
0.10	4.918	4.899	4.886	4.874	4.870	4.868	4.869	4.875	4.883	4.896	4.913	4.933	4.955
0.07	4.958	4.940	4.928	4.917	4.913	4.912	4.914	4.920	4.929	4.943	4.961	4.982	5.004
0.05	4.998	4.980	4.969	4.958	4.955	4.955	4.957	4.963	4.974	4.989	5.006	5.028	5.052
0.03	5.059	5.042	5.031	5.022	5.019	5.019	5.023	5.030	5.041	5.057	5.075	5.098	5.123
0.02	5.106	5.090	5.079	5.070	5.068	5.068	5.072	5.080	5.092	5.108	5.127	5.151	5.178
0.01	5.180	5.163	5.153	5.146	5.144	5.144	5.149	5.158	5.171	5.188	5.207	5.233	5.259
0.007	5.213	5.197	5.187	5.180	5.178	5.179	5.184	5.193	5.207	5.224	5.244	5.269	5.296
0.005	5.241	5.225	5.216	5.209	5.208	5.209	5.214	5.224	5.238	5.255	5.275	5.300	5.327
0.003	5.279	5.263	5.254	5.248	5.246	5.249	5.255	5.264	5.278	5.296	5.317	5.343	5.370
0.002	5.308	5.290	5.281	5.275	5.273	5.276	5.282	5.292	5.306	5.325	5.346	5.372	5.399
0.001	5.341	5.326	5.317	5.312	5.311	5.313	5.320	5.330	5.345	5.363	5.385	5.410	5.439

Series A, part 2. $m_{K_2Ph}=m_{KHPh}$ (no KCl)

0.10	4.951	4.933	4.919	4.908	4.904	4.902	4.903	4.909	4.918	4.931	4.949	4.969	4.991
0.07	4.991	4.972	4.960	4.950	4.946	4.944	4.947	4.953	4.963	4.977	4.995	5.017	5.040
0.05	5.029	5.011	4.999	4.990	4.987	4.987	4.989	4.996	5.007	5.022	5.040	5.062	5.086
0.03	5.089	5.071	5.059	5.051	5.048	5.048	5.052	5.060	5.071	5.087	5.107	5.129	5.154
0.02	5.133	5.116	5.105	5.098	5.095	5.096	5.099	5.109	5.120	5.136	5.156	5.179	5.205
0.01	5.201	5.185	5.175	5.169	5.167	5.168	5.172	5.181	5.194	5.211	5.232	5.257	5.283
0.007	5.233	5.217	5.207	5.201	5.198	5.199	5.204	5.214	5.228	5.244	5.266	5.291	5.318
0.005	5.259	5.243	5.233	5.227	5.226	5.228	5.233	5.243	5.257	5.274	5.294	5.320	5.347
0.003	5.294	5.278	5.269	5.263	5.261	5.264	5.270	5.280	5.294	5.311	5.333	5.359	5.386
0.002	5.318	5.302	5.293	5.288	5.286	5.289	5.295	5.305	5.319	5.337	5.359	5.385	5.413
0.001	5.346	5.331	5.327	5.322	5.320	5.323	5.330	5.340	5.355	5.373	5.395	5.422	5.450

TABLE 11.—pH *values of aqueous solutions of acid potassium phthalate, dipotassium phthalate and potassium chloride from 0° to 60° C for rounded concentrations*

Series B, part 1. $m_{K_2Ph} = 1.5\ m_{KHPh} = 1.5\ m_{KCl}$

Molality of acid potassium phthalate	Temperature in degrees centigrade												
	0	5	10	15	20	25	30	35	40	45	50	55	60
Moles of solute per 1,000 g of water													
0.07	5.110	5.091	5.078	5.069	5.063	5.061	5.063	5.068	5.077	5.090	5.107	5.127	5.150
0.05	5.147	5.129	5.117	5.107	5.102	5.101	5.103	5.109	5.119	5.133	5.151	5.172	5.195
0.04	5.173	5.155	5.143	5.134	5.129	5.128	5.131	5.138	5.149	5.163	5.180	5.202	5.225
0.02	5.255	5.237	5.226	5.219	5.214	5.215	5.218	5.226	5.238	5.252	5.272	5.295	5.319
0.01	5.330	5.313	5.303	5.296	5.294	5.294	5.298	5.307	5.318	5.335	5.355	5.379	5.405
0.008	5.352	5.336	5.326	5.318	5.316	5.317	5.322	5.331	5.344	5.360	5.381	5.404	5.430
0.005	5.396	5.380	5.370	5.363	5.361	5.361	5.368	5.378	5.390	5.407	5.428	5.452	5.479
0.004	5.415	5.398	5.388	5.383	5.380	5.382	5.387	5.397	5.410	5.427	5.449	5.474	5.500
0.002	5.464	5.449	5.439	5.434	5.432	5.434	5.440	5.450	5.464	5.482	5.503	5.529	5.556
0.001	5.504	5.489	5.480	5.475	5.473	5.476	5.482	5.493	5.507	5.524	5.546	5.572	5.600

Series B, part 2. $m_{K_2Ph} = 1.5\ m_{KHPh}$ (no KCl)

0.07	5.135	5.116	5.103	5.094	5.088	5.086	5.088	5.093	5.103	5.116	5.133	5.154	5.176
0.05	5.171	5.153	5.141	5.132	5.127	5.126	5.128	5.134	5.144	5.158	5.176	5.198	5.221
0.04	5.196	5.178	5.167	5.158	5.153	5.153	5.156	5.162	5.173	5.188	5.206	5.227	5.251
0.02	5.275	5.258	5.246	5.239	5.236	5.236	5.241	5.248	5.260	5.275	5.294	5.317	5.342
0.01	5.348	5.331	5.321	5.312	5.311	5.312	5.317	5.326	5.338	5.354	5.376	5.399	5.425
0.008	5.369	5.353	5.343	5.329	5.333	5.334	5.340	5.349	5.361	5.377	5.398	5.422	5.449
0.005	5.410	5.394	5.384	5.381	5.376	5.376	5.382	5.393	5.405	5.422	5.443	5.468	5.495
0.004	5.428	5.411	5.402	5.396	5.394	5.396	5.401	5.411	5.424	5.442	5.463	5.488	5.505
0.002	5.474	5.459	5.450	5.444	5.443	5.445	5.451	5.461	5.475	5.493	5.515	5.540	5.568
0.001	5.512	5.497	5.488	5.481	5.481	5.484	5.490	5.502	5.515	5.533	5.555	5.580	5.608

TABLE 12.—pH *values of aqueous solutions of acid potassium phthalate, dipotassium phthalate and potassium chloride from 0° to 60° C for rounded concentrations*

Series C, part 1. $m_{K_2Ph} = 2.0\ m_{KHPh} = 2.0\ m_{KCl}$

Molality of acid potassium phthalate	Temperature in degrees centigrade												
	0	5	10	15	20	25	30	35	40	45	50	55	60
Moles of solute per 1,000 g of water													
0.05	5.252	5.233	5.221	5.211	5.206	5.204	5.206	5.211	5.221	5.234	5.252	5.272	5.294
0.04	5.277	5.258	5.246	5.237	5.231	5.230	5.232	5.239	5.248	5.262	5.280	5.301	5.325
0.03	5.309	5.291	5.279	5.271	5.266	5.265	5.268	5.275	5.285	5.300	5.318	5.339	5.363
0.02	5.356	5.339	5.327	5.319	5.315	5.316	5.319	5.326	5.337	5.353	5.371	5.393	5.418
0.01	5.431	5.417	5.406	5.399	5.396	5.396	5.401	5.410	5.422	5.437	5.457	5.481	5.507
0.005	5.502	5.486	5.476	5.470	5.467	5.469	5.474	5.482	5.495	5.512	5.533	5.557	5.584
0.004	5.522	5.506	5.496	5.490	5.487	5.489	5.494	5.504	5.517	5.534	5.554	5.579	5.605
0.003	5.546	5.529	5.519	5.514	5.511	5.513	5.519	5.528	5.542	5.559	5.580	5.605	5.631
0.002	5.576	5.560	5.551	5.545	5.542	5.544	5.550	5.560	5.574	5.591	5.613	5.638	5.665
0.001	5.618	5.602	5.592	5.588	5.584	5.589	5.595	5.605	5.619	5.637	5.659	5.685	5.713

Series C, part 2. $m_{K_2Ph} = 2.0\ m_{KHPh}$ (no KCl)

0.05	5.272	5.253	5.241	5.231	5.226	5.225	5.226	5.233	5.241	5.255	5.273	5.293	5.316
0.04	5.296	5.277	5.265	5.256	5.251	5.250	5.252	5.259	5.269	5.283	5.301	5.322	5.345
0.03	5.328	5.310	5.298	5.290	5.286	5.285	5.287	5.294	5.305	5.319	5.338	5.360	5.383
0.02	5.374	5.351	5.345	5.337	5.333	5.334	5.337	5.345	5.355	5.371	5.390	5.412	5.437
0.01	5.449	5.432	5.422	5.415	5.411	5.412	5.417	5.425	5.438	5.453	5.473	5.497	5.523
0.005	5.515	5.499	5.488	5.482	5.479	5.482	5.487	5.495	5.508	5.525	5.546	5.570	5.597
0.004	5.533	5.517	5.507	5.501	5.499	5.501	5.506	5.516	5.528	5.545	5.566	5.591	5.618
0.003	5.555	5.540	5.530	5.524	5.522	5.524	5.530	5.539	5.553	5.570	5.592	5.616	5.644
0.002	5.585	5.569	5.560	5.554	5.552	5.553	5.559	5.569	5.583	5.601	5.622	5.647	5.675
0.001	5.624	5.609	5.600	5.594	5.593	5.596	5.602	5.612	5.626	5.644	5.672	5.691	5.720

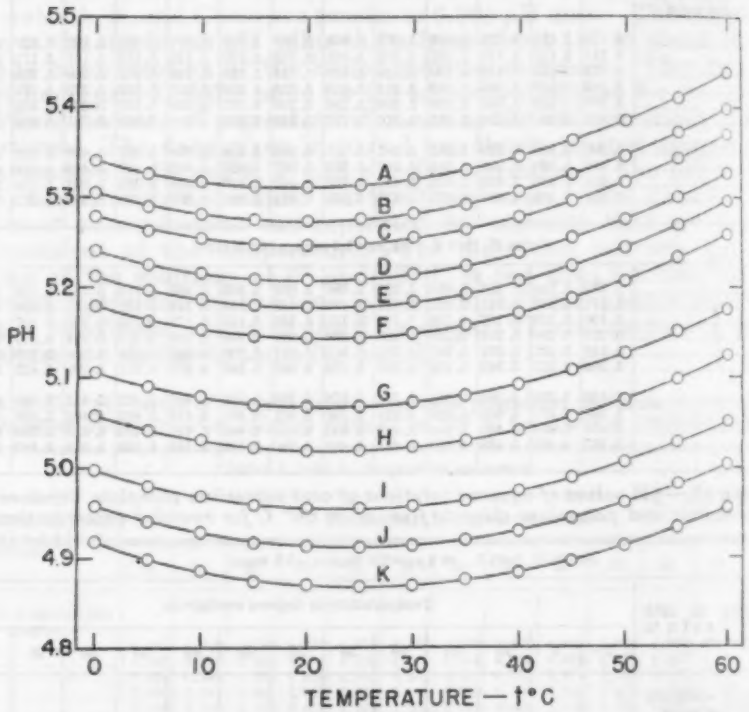

FIGURE 6.—*Plots of the* pH *values of phthalate-chloride solutions whose compositions correspond to those of series A against the temperature in degrees centigrade.*

A, 0.001 *M* KHPh; *B*, 0.002 *M* KHPh; *C*, 0.003 *M* KHPh; *D*, 0.005 *M* KHPh; *E*, 0.007 *M* KHPh; *F*, 0.01 *M* KHPh; *G*, 0.02 *M* KHPh; H, 0.03 *M* KHPh; *I*, 0.05 *M* KHPh; *J*, 0.07 *M* KHPh; *K*, 0.10 *M* KHPh.

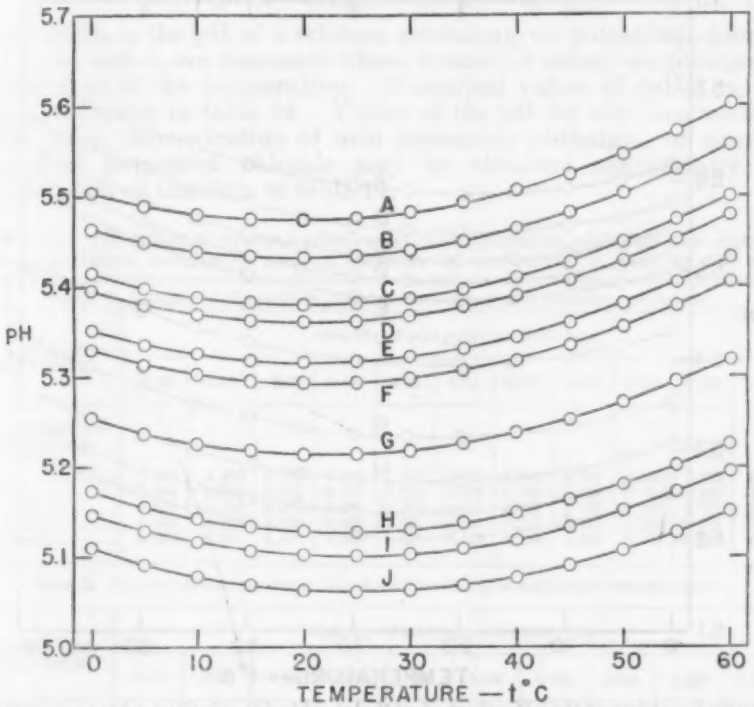

FIGURE 7.—*Plots of the* pH *values of phthalate-chloride solutions whose compositions correspond to those of series B against the temperature in degrees centigrade.*

A, 0.001 *M* KHPh; *B*, 0.002 *M* KHPh; *C*, 0.004 *M* KHPh; *D*, 0.005 *M* KHPh; *E*, 0.008 *M* KHPh; *F*, 0.01 *M* KHPh; *G*, 0.02 *M* KHPh; *H*, 0.04 *M* KHPh; *I*, 0.05 *M* KHPh; *J*, 0.0 *M* KHPh.

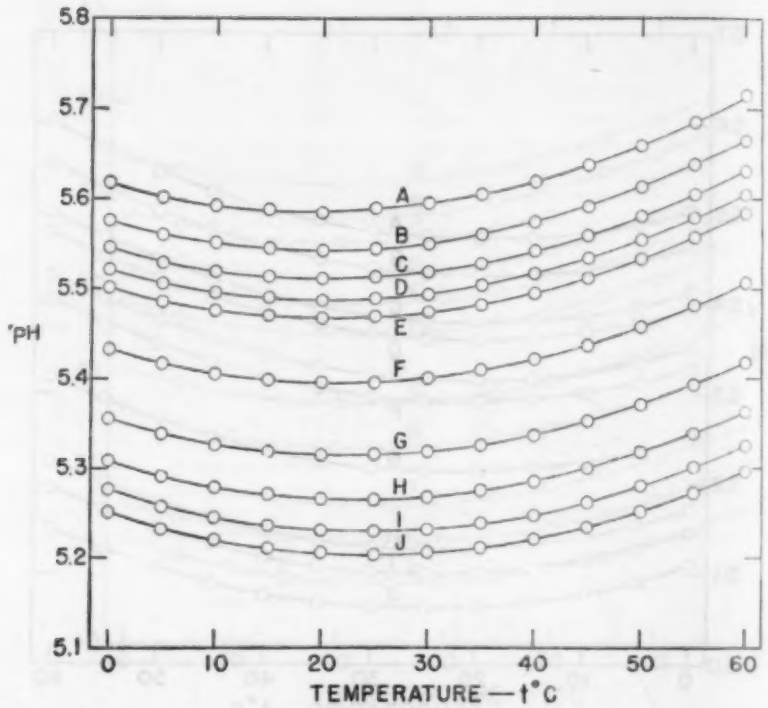

FIGURE 8.—*Plots of the* pH *values of phthalate-chloride solutions whose compositions correspond to those of series C against the temperature in degreees centigrade.*

A, 0.001 *M* KHPh; *B*, 0.002 *M* KHPh; *C*, 0.003 *M* KHPh; *D*, 0.004 *M* KHPh; *E*, 0.005 *M* KHPh; *F*, 0.01 *M* KHPh; *G*, 0.02 *M* KHPh; *H*, 0.03 *M* KHPh; *I*, 0.04 *M* KHPh· *J*, 0.05 *M* KHPh.

In table 13, the pH values at 25° C are given for solutions of different buffer ratios containing various amounts of potassium chloride. The data are shown plotted against the molality of potassium chloride in figures 9, 10, and 11. The addition of potassium chloride has a similar effect on the pH values for the three different buffer ratios and is more marked for dilute than for concentrated solutions. The pH of these solutions may be computed as a function of the molality of potassium chloride by the equation.

$$pH=(pH)_0+\alpha_1 m_{KCl}+\alpha_2 m^2_{KCl}+\alpha_3 m^3_{KCl}, \quad (39)$$

where $(pH)_0$ is the pH of a solution containing no potassium chloride and α_1, α_2, and α_3 are constants whose numerical values are practically independent of the temperature. Numerical values of $(pH)_0$, α_1, α_2, and α_3 are given in table 14. Values of the pH for any intermediate buffer ratio, concentration of acid potassium phthalate, or concentration of potassium chloride may be obtained conveniently by interpolation of the data of table 14.

TABLE 13.—pH *values of aqueous solutions of acid potassium phthalate and dipotassium phthalate containing various amounts of potassium chloride at 25° C*

Series A. Molality of dipotassium phthalate=molality of acid potassium phthalate

Molality of potassium chloride	Molality of acid potassim phthalate										
	0.10	0.07	0.05	0.03	0.02	0.01	0.007	0.005	0.003	0.002	0.001
Moles of solute per 1,000 g of water											
0.10	4.868	4.899	4.927	4.956	4.990	5.021	5.031	5.040	5.048	5.052	5.056
0.05	4.884	4.920	4.955	5.002	5.034	5.078	5.093	5.106	5.118	5.126	5.132
0.02	4.895	4.934	4.973	5.029	5.068	5.125	5.147	5.166	5.185	5.197	5.208
0.01	4.899	4.939	4.980	5.039	5.081	5.144	5.170	5.192	5.219	5.235	5.252
0.00	4.902	4.945	4.987	5.049	5.096	5.168	5.199	5.228	5.265	5.291	5.326

Series B. Molality of dipotassium phthalate=1.5×molality of acid potassium phthalate

Molality of potassium chloride	Molality of acid potassium phthalate									
	0.07	0.05	0.04	0.02	0.01	0.008	0.006	0.004	0.002	0.001
Moles of solute per 1,000 g of water										
0.10	5.051	5.079	5.098	5.149	5.185	5.198	5.209	5.213	5.225	5.231
0.05	5.068	5.101	5.123	5.186	5.236	5.249	5.271	5.278	5.296	5.307
0.02	5.079	5.115	5.140	5.215	5.277	5.294	5.325	5.336	5.364	5.382
0.01	5.082	5.120	5.147	5.225	5.294	5.313	5.349	5.362	5.398	5.420
0.00	5.086	5.126	5.153	5.236	5.312	5.334	5.378	5.396	5.445	5.485

Series C. Molality of dipotassium phthalate=2.0×molality of acid potassium phthalate

Molality of potassium chloride	Molality of acid potassium phthalate									
	0.05	0.04	0.03	0.02	0.01	0.005	0.004	0.003	0.002	0.001
Moles of solute per 1,000 g of water										
0.10	5.186	5.204	5.228	5.258	5.299	5.322	5.333	5.340	5.347	5.354
0.05	5.204	5.225	5.254	5.292	5.346	5.379	5.395	5.405	5.417	5.429
0.02	5.216	5.240	5.271	5.316	5.382	5.426	5.449	5.464	5.482	5.502
0.01	5.220	5.245	5.278	5.324	5.396	5.446	5.472	5.490	5.513	5.539
0.00	5.225	5.250	5.285	5.334	5.412	5.481	5.501	5.524	5.554	5.596

TABLE 14.—*Values of the constants* $(pH)_0, \alpha_1, \alpha_2$, *and* α_3 *in the equation* $pH=(pH)_0+\alpha_1 m_{KCl}+\alpha_2 m^2_{KCL}+\alpha_3 m^3_{KCL}$ *which gives the* pH *of phthalate solutions as a function of the molality of potassium chloride*

Molality of acid potassium phthalate	$(pH)_0$	$-\alpha_1$	α_2	$-\alpha_3$
Series A, Molality of dipotassium phthalate = molality of acid potassium phthalate				
Moles of solute /1,000 g of water				
0.001	5.326	8.107	115.39	613.2
.002	5.291	6.116	75.43	381.8
.003	5.265	5.064	56.20	273.0
.005	5.228	3.792	35.09	159.7
.007	5.199	3.064	23.97	101.4
.01	5.168	2.490	17.72	74.3
.02	5.096	1.55	7.46	25.8
.03	5.049	1.05	3.11	19.3
.05	4.987	0.742	2.63	12.2
.07	4.945	.609	0.61	8.0
.10	4.902	.461	−1.00	3.5
Series B, Molality of dipotassium phthalate = 1.5 × molality of acid potassium phthalate				
0.001	5.485	6.956	92.10	479.4
.002	5.445	5.114	56.33	271.9
.004	5.396	3.629	32.87	148.7
.005	5.378	3.111	24.64	123.2
.008	5.334	2.232	12.54	38.2
.01	5.312	1.916	9.36	29.0
.02	5.236	1.170	3.30	12.2
.04	5.153	0.656	1.12	5.13
.05	5.126	.550	0.502	4.20
.07	5.086	.366	.101	2.73
Series C, Molality of dipotassium phthalate = 2.0 × molality of acid potassium phthalate				
0.001	5.596	6.156	75.53	383.0
.002	5.554	4.435	44.23	205.8
.003	5.524	3.611	31.62	139.1
.004	5.501	3.064	23.97	101.4
.005	5.481	2.680	19.01	83.0
.01	5.412	1.662	8.39	30.7
.02	5.334	0.985	3.61	13.5
.03	5.285	.756	2.50	6.5
.04	5.250	.635	2.10	2.7
.05	5.225	.576	1.06	0.9

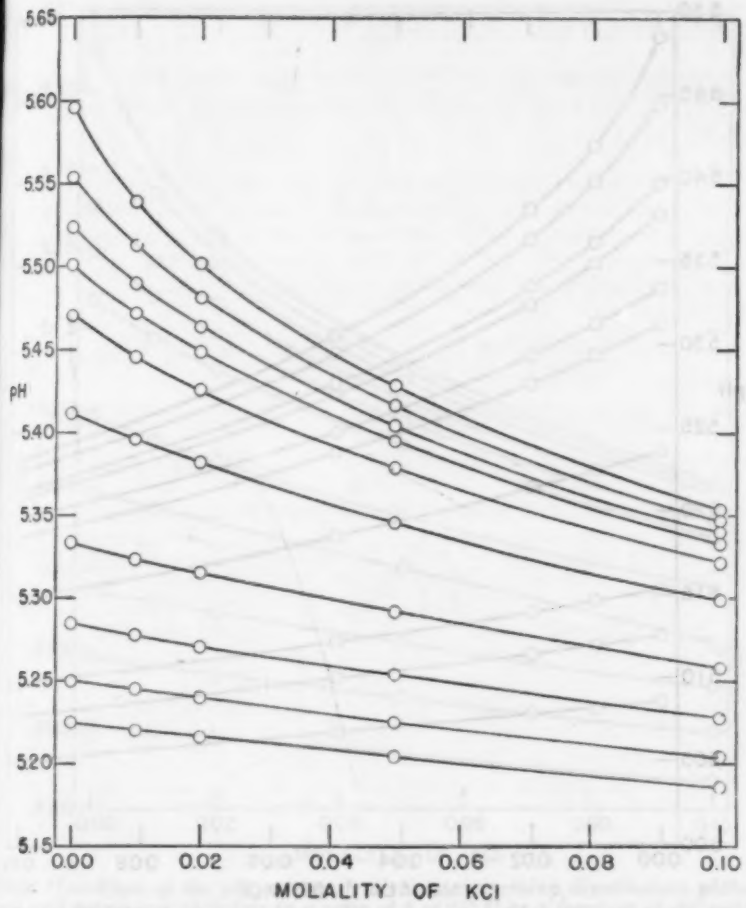

FIGURE 9.—*Plots of the* pH *values of solutions containing dipotassium phthalate and acid potassium phthalate in unit ratio at 25° C as a function of the molality of potassium chloride.*

The curves reading from the top correspond to 0.001, 0.002, 0.003, 0.005, 0.007, 0.01, 0.02, 0.03, 0.05, 0.07, and 0.10 molal acid potassium phthalate.

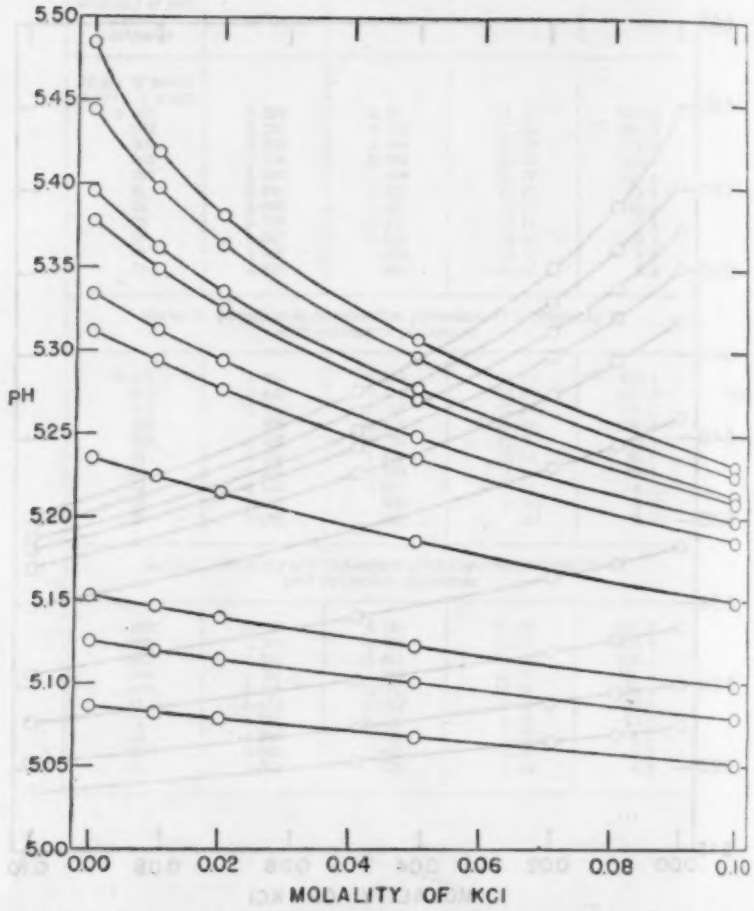

FIGURE 10.—*Plots of the* pH *values of solutions containing dipotassium phthalate and acid potassium phthalate in the ratio of 1.5 at 25° C as a function of the molality of potassium chloride.*

The curves reading from the top correspond to 0.001, 0.002, 0.004, 0.005, 0.01, 0.02, 0.04, 0.05, and 0.07 molal acid potassium phthalate.

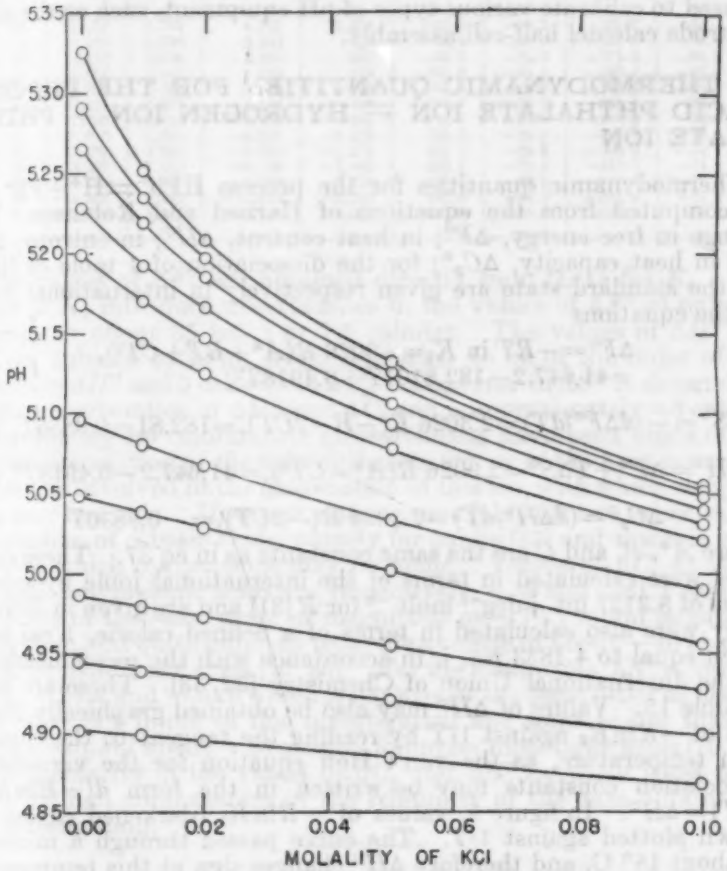

FIGURE 11.—*Plots of the* pH *values of solutions containing dipotassium phthalate and acid potassium phthalate in a ratio of 2 at 25° C as a function of the molality of potassium chloride.*

The curves reading from the top correspond to 0.001, 0.002, 0.003, 0.004, 0.005, 0.01, 0.02, 0.03, 0.04, and 0.05 molal acid potassium phthalate.

Each solution may be used as a standard for pH. It is proposed that they be prepared from the NBS Standard Sample 84a, of acid potassium phthalate, carbonate-free potassium hydroxide, and potassium chloride which meet the specifications of the American Chemical Society, and distilled water of pH 6.7 to 7.3 having a specific conductance of not over 1.0×10^{-6} mho. The solutions may be used to calibrate various types of pH equipment, such as the glass electrode calomel half-cell assembly.

VI. THERMODYNAMIC QUANTITIES FOR THE PROCESS ACID PHTHALATE ION ⇌ HYDROGEN ION + PHTHALATE ION

Thermodynamic quantities for the process $HPh^- \rightleftharpoons H^+ + Ph^=$ can be computed from the equations of Harned and Robinson. The change in free energy, ΔF°; in heat content, ΔH°; in entropy, ΔS°; and in heat capacity, ΔC_p°; for the dissociation of 1 mole of HPh^- for the standard state are given respectively in international joules by the equations

$$\Delta F^\circ = -RT \text{ in } K_2 = 2.3026\, R(A^* + BT + CT^2),$$
$$= 41{,}647.2 - 182.8101T + 0.4918T^2, \quad (40)$$

$$\Delta S^\circ = -(d\Delta F^\circ/dT) = 2.3026\, R(-B - 2CT), = 182.81 - 0.9836T \quad (41)$$

$$\Delta H^\circ = \Delta F^\circ + T\Delta S^\circ = 2.3026\, R(A^* - CT^2), = 41{,}647.2 - 0.4918T^2, \quad (42)$$

$$\Delta C_p^\circ = (d\Delta H^\circ/dT) = 2.3026\, R(-2CT), = -0.9836T, \quad (43)$$

where A^*, B, and C are the same constants as in eq 37. These quantities were calculated in terms of the international joule by using a value of 8.3127 int. j deg^{-1} mole^{-1} for R [31] and are given in table 15. They were also calculated in terms of a defined calorie, 1 cal being taken equal to 4.1833 int. j, in accordance with the recommendation of the International Union of Chemistry [32, 33]. These are listed in table 15. Values of ΔH° may also be obtained graphically from a plot of $-R\ln K_2$ against $1/T$ by reading the tangent to the curve at each temperature, as the van't Hoff equation for the variation of dissociation constants may be written in the form $d(-R\ln K_2)/d(1/T) = \Delta H^\circ$. In figure 5, values of $-R\ln K_2$ (darkened circles) are shown plotted against $1/T$. The curve passed through a minimum at about 18° C, and therefore ΔH° changes sign at this temperature. Values of ΔH° determined graphically are not as accurate as those determined by eq 42, owing to the difficulty of reading with accuracy the tangent to the curve. The values of ΔC_p° increase slightly with the temperature, as predicted by a semiempirical equation derived by Moelwyn-Hughes [34]. Values of ΔF° and ΔS° also increase with respect to temperature.

TABLE 15.—*Thermodynamic data from 0° to 60° C for the dissociation of the acid phthalate ion into hydrogen and phthalate ions*

Temperature	$\Delta F°$		$\Delta H°$		$\Delta S°$		$\Delta C_p°$	
°C	*Int. j*	*cal*	*Int. j*	*cal*	*Int. j*	*cal*	*Int. j*	*cal*
0	28,407	6,791	4,951	1,183	−85.9	−20.5	−288.7	−64.2
5	28,849	6,896	3,595	859	−90.8	−21.7	−273.6	−65.4
10	29,315	7,008	2,215	529	−95.7	−22.9	−278.5	−66.6
15	29,806	7,125	810	194	−100.6	−24.1	−283.4	−67.8
20	30,321	7,248	−620	−148	105.5	−25.2	−288.4	−68.9
25	30,861	7,377	−2,074	−496	110.5	−26.4	−293.3	−70.1
30	31,426	7,512	−3,552	−849	115.4	−27.6	−298.2	−71.3
35	32,015	7,653	−5,055	−1,208	120.3	−28.8	−303.1	−72.5
40	32,629	7,800	−6,583	−1,574	125.2	−29.9	−308.0	−73.6
45	33,267	7,952	−8,136	−1,945	130.1	−31.1	−312.9	−74.8
50	33,930	8,111	−9,713	−2,322	135.1	−32.3	−317.9	−76.0
55	34,618	8,275	−11,314	−2,705	140.0	−33.5	−322.8	−77.2
60	35,330	8,445	−12,940	−3,093	144.9	−34.6	−327.7	−78.3

The values of $\Delta F°$ are obtained directly from those for K_2. The errors in K_2 introduce uncertainties in the values of $\Delta F°$ of only 0.1 percent, or about 35 int. j or 7.5 calories. The values of $\Delta H°$ and $\Delta C_p°$ are subject to large error, estimated to be of the order of 100 calories in $\Delta H°$ and 3 calories in $\Delta C_p°$. The error in $\Delta S°$ is determined by the uncertainties in $\Delta H°$ and $\Delta C_p°$ and is approximately 0.3 calorie. Unfortunately no calorimetric measurements have been made of the heat of dissociation of the acid phthalate ion, or of the heat capacities of the ions involved in the dissociation of this ion, with which comparisons may be made. However, data are available for two other second dissociation of dibasic acids, namely for oxalic [35] and malonic acids [8], with which comparisons may be made. Values of $\Delta C_p°$ at 25° C for oxalic and malonic acids are, respectively, −59 and −61.3 calories, which are of the same order of magnitude as −70.1 found in this investigation and quite different from the average of about −40 calories found for monobasic acids [10, 36]. For the same acids, $\Delta S°$ is, respectively, −24.4 and −30.0 which is likewise of the same order of magnitude as −26.4 found in this investigation and some higher than an average value of about −20 calories found for monobasic acids [10, 36]. The similarity in the values of $\Delta C_p°$ and $\Delta S°$ for these three acids offers indirect confirmation of the reliability of the data obtained in this investigation.

The authors are indebted to Gladys D. Pinching for making a part of the calculations and drawings and to Cyrus G. Malmberg for measuring the conductance of the water used in the preparation of the buffer solutions.

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RESEARCH PAPER RP1679

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IMPACT STRENGTH OF NYLON AND OF SISAL ROPES

By Sanford B. Newman and Helen G. Wheeler

ABSTRACT

Static and impact tests were made on spliced specimens of 7/16-inch-diameter three-strand nylon rope and 9/16-inch-diameter, four-strand, sisal rope.

The stretch of the ropes under impact and static loading up to failure was measured, and from these data energy-stretch behavior was determined.

It was found that the energy required to cause failure under impact loading was greater than the energy required to cause failure under static loading. The stretch of the rope at failure was practically the same under impact and static loading.

The results of these tests indicate that energy values computed from static tests of these ropes give a safe estimate of the performance of the rope under impact loading.

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I. INTRODUCTION

Although it is customary to test the strength of rope in machines that apply the load at a slow rate, ropes are expected to withstand impact loads in important uses. Safety ropes used by structural workers, shipbuilders, and lumbermen, for example, are expected to absorb the shock if the workman falls. His life may depend upon the impact energy absorbed by the rope. Similarly, mountain climbers are dependent upon the impact strength of their ropes. The work

reported in this paper was undertaken to supply accurate information as to the strength and limitations of ropes under consideration by the Office of the Quartermaster General for the use of mountain troops. The results are equally applicable to related uses of ropes.

Adequate data had previously been furnished by the Bureau as to the energy that can be absorbed by a rope, as computed from the load-stretch curves obtained from a specimen loaded at a comparatively slow rate of speed in a testing machine. It was realized that the energy-absorbing capacity of the rope might be substantially different under impact loading.

The most severe impact to which a climbing rope can be subjected would be applied by a man falling from a position directly above the point of attachment of the rope, with the rope fully extended, and dropping through a distance equal to twice the length of the rope. It was therefore suggested that nylon rope and sisal rope, representing fibers and sizes commonly in use, be tested to determine energy and stretch behavior under impact and static loading. The lengths of samples suggested for test were 5 ft and 10 ft; the impact load to be dropped through a distance equal to twice the length of the ropes. For the purposes of this investigation, failure was defined as the breaking of one or more strands at the maximum load sustained in a static test, or the breaking of one or more strands under the impact load applied in an impact test.

II. SPECIMENS

1. STATIC TESTS

Four 120-ft coils of $\frac{7}{16}$-in.-diameter three-strand nylon climbing rope of type 300 bright nylon yarn and one 53-lb coil of $\frac{7}{16}$-in.-diameter four-strand, sisal rope, supplied by the Office of the Quartermaster General, were used for these tests. The specimens were conditioned in an atmosphere of 65 $\pm$2-percent relative humidity and 70° $\pm$2° F for at least 72 hours preceding the tests.

Three spliced specimens of sisal rope and three spliced specimens of nylon rope were prepared for determination of breaking strength, load-stretch relationship, and stretch at failure under static loading. Each was a conventional breaking-strength specimen having an eye splice at each end and a free length of approximately 2 ft. The splices consisted of three full tucks and two tucks made with half the yarns in each strand. The over-all lengths and the free lengths of the sisal and the nylon specimens were measured under no load while they were in the testing machine ready for test. The lengths are given in table 1.

TABLE 1.—*Over-all length and free length of static specimens*

Specimen	Over-all length	Free length *
	in.	*in.*
Sisal 1-1a	48.7	21.9
Sisal 1-1b	48.6	22.9
Sisal 1-1c	48.4	22.6
Nylon 1-2a	48.3	24.4
Nylon 1-2b	48.5	24.1
Nylon 1-2c	48.4	23.9

* Defined as the distance between a point ½ in. in from the last tuck of 1 splice to a point ½ in. in from the last tuck of the other splice.

2. IMPACT TESTS

Fourteen spliced specimens of nylon rope and 15 spliced specimens of sisal rope from the same coils as were used for the static tests with 5-ft nominal over-all length were used for impact test. In addition, 12 spliced specimens of each kind of rope with 10-ft nominal over-all length were tested. These specimens also consisted of a free length with an eye splice at each end. The splices of the impact-test and static-test specimens were carefully made so as to be very nearly alike.

The specimen lengths were measured by determining the distance L shown in figure 1. The specimen was suspended from an eyebolt by means of snap links passed through one eye, and the weight pan was fastened to the other eye by means of other snap links. The weight pan and its connecting snap links weighed 14 lb. An appreciable amount of creep was exhibited by the nylon specimens, and their lengths were taken 5 minutes after the weight pan was attached. No creep was observed in the sisal specimens. The lengths of the four groups of specimens are given in table 2.

TABLE 2.—*Lengths of impact specimens*

[All specimens measured under a load of 14 lb.]

Specimens	Maximum	Minimum	Average
	in.	in.	in.
5-ft sisal:			
Over-all length	60.1	58.4	59.2
Free length	32.5	29.4	30.2
10-ft sisal:			
Over-all length	121.2	118.5	119.7
Free length	92.0	89.5	91.0
5-ft nylon:			
Over-all length	62.4	60.2	61.3
Free length	36.6	34.0	35.3
10-ft nylon:			
Over-all length	126.7	121.6	123.6
Free length	99.5	95.5	96.9

III. TESTING PROCEDURE

1. STATIC TESTS

The static-test specimens were loaded in a horizontal hydraulic testing machine of 100,000-lb capacity, the 20,000-lb scale range being used. The specimens were fastened to the heads of the testing machine by means of a 3-in.-diameter pin passed through the eye at each end. The speed of the moving head of the testing machine was 1 in./min during the tests. Each specimen was loaded until failure occurred.

To determine the load-stretch relationship, stretch readings under loads from zero to the maximum load were taken for the free length [1] and for each eye and splice of each specimen by means of a graduated scale held parallel to the specimen and with the end of the scale tangent to the pin through the eye at the set head of the testing machine. Stretch readings were taken at both ends of the free length and at the end of the specimen at the moving head of the testing machine.

[1] Defined as the distance between a point ½ in. in from the last tuck of 1 splice to a point ½ in. in from the last tuck of the other splice.

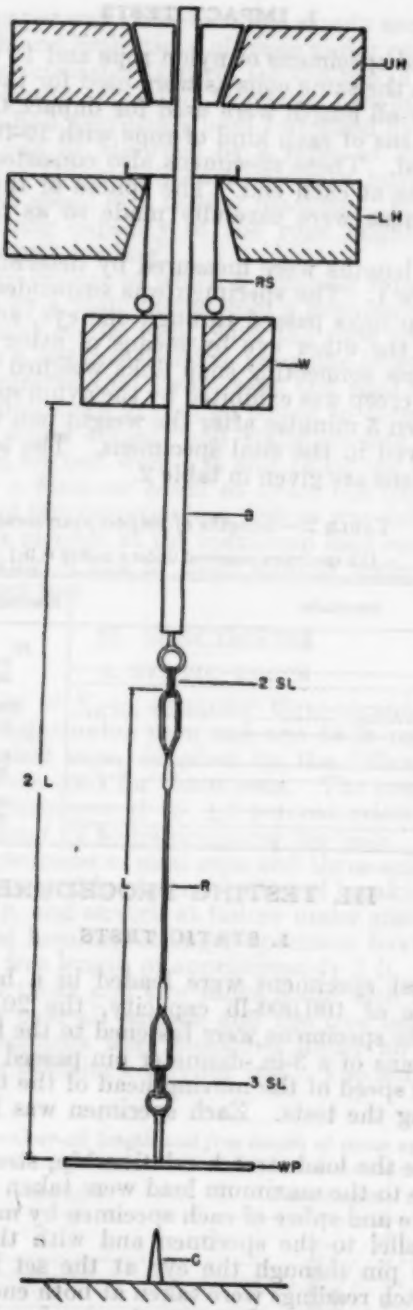

FIGURE 1.—*Schematic diagram of impact-test setup.*

Legend: *UH*, Upper head; *LH*, lower head; *RS*, release string; *W*, weight; *B*, bar; *2SL*, two snap links; *R*, rope; *3SL*, three snap links; *WP*, weight pan; *C*, clay column; *L*, length of specimen; *2L*, twice the length of the specimen.

2. IMPACT TESTS

A large testing machine was found convenient for mounting and adjusting the fixtures used in the impact tests. Figure 1 shows schematically the fixtures used for applying impact loads to the spliced specimens. A 1⅝-in. steel bar (*B*) was gripped in the jaws of the upper head (*UH*) of the large testing machine and passed through the lower head (*LH*). An eyebolt screwed into the bar was attached to the specimen (*R*) by means of two snap links (2 *SL*) passed through one eye. The other eye of the specimen was attached to the eyebolt of the weight pan (*WP*) by means of three snap links. The weight (*W*) consisted of steel disks with a 4-in. hole through their centers. The disks were bolted together, passed over the bar, and suspended by means of a ¼-in. diameter sash-cord release string (*RS*), which was strung over two pins in the lower head.

The lower head was then raised or lowered until the distance (2*L*) from the bottom of the weight to the top of the weight pan, was adjusted to twice the length of the specimen. The weight was dropped by cutting the release string. Each specimen was subjected to one impact load.

The instantaneous clearance at impact between the weight pan and the floor was obtained from the clay column (*C*). The distance from the bottom of the weight pan to the floor was measured before test, and the height of the clay column was measured after the impact load had been applied. The difference between the two measurements is the stretch of the specimen under the impact load. The weight required to cause complete failure of the specimen or that needed to break one or more strands was determined. Where all of the strands of a specimen parted it was impossible to determine stretch under load.

IV. RESULTS

1. STATIC TESTS

From the load-stretch data obtained from the static tests of the specimens, the load-stretch relationships were calculated separately for each eye and splice length and for the free length of each specimen. The test results of the three sisal specimens and the three nylon specimens were averaged.

In figures 2 and 3 the stretch, in inches, of the eyes and splices of the sisal and the nylon static-test specimens have been plotted against load. The curves have been drawn through the average stretch values. The individual stretch-load curves for each eye and splice length were also drawn, and the area under each curve was determined by graphical integration. This area gives the energy absorbed by each eye and splice. The energy values in inch-pounds are presented in table 3.

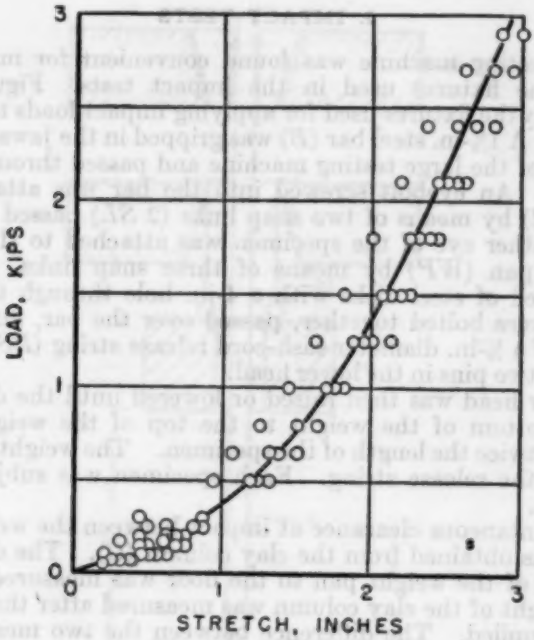

FIGURE 2.—*Load-stretch curve for eye and splice lengths of sisal static-test specimens*

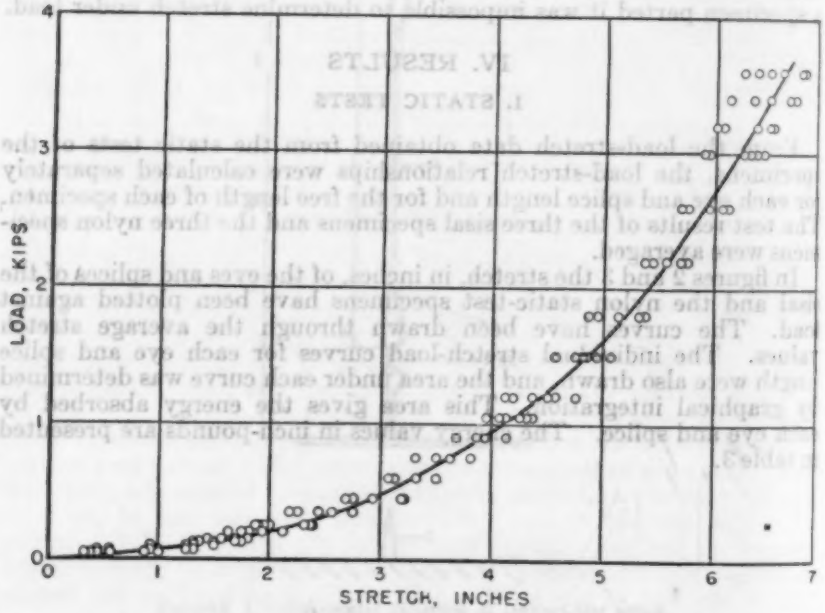

FIGURE 3.—*Load-stretch curve for eye and splice lengths of nylon static-test specimens.*

TABLE 3.—*Results of static tests*

[Speed of moving head of testing machine, 1 in./min.]

	Specimen			Average	Specimen			Average
	1-1a	1-1b	1-1c		1-2a	1-2b	1-2c	
	Sisal, ⅜ in. in diameter				Nylon, ⅜ in. in diameter			
Breaking load, lb	2,800	3,230	2,920	2,980	4,320	4,240	4,050	4,200
Failure	End of splice	End of splice	End of splice		In the splice	In the splice	In the splice	
Elongation of free length at failure, percent	17.8	17.7	18.9	18.1	53.0	53.7	51.3	52.7
Static energy:								
Free length, in.-lb/in	161	196	191	182	616	583	566	588
One eye and splice, in.-lb	2,670	3,330	2,800	2,970	8,350	8,510	7,670	7,990
Other eye and splice, in.-lb	2,900	3,270	2,880		8,090	7,750	7,540	

In figures 4 and 5 the percentage of stretch of the free lengths of the sisal and the nylon static-test specimens have been plotted against load. The curves have been drawn through the average stretch values. The individual stretch-load curves for each free length were also drawn, and the area under each curve was determined by graphical integration. This area gives the energy absorbed by each unit length of free length of the specimen. The energy values in inch-pounds per inch are presented in table 3.

The average over-all lengths of the 5-ft impact specimens and of the 10-ft impact specimens of each kind of rope were determined, and static-load–stretch curves were drawn for specimens having these over-all lengths. It was assumed that the eye-and-splice part of the hypothetical and the static specimens would have the same load-stretch relationship, and that the free length part of the two kinds of specimens would have equal stretch per unit length. These load-stretch curves are given in figure 6.

By graphical integration of the static load-stretch curves for the average-length impact specimens shown in figure 6, the energy absorption for various amounts of stretch was obtained. This computed static-energy–stretch relationship is given by the lines in figures 7, 8, 9, and 10. The energy values corresponding to the stretch at failure of the first strand are the ordinates at the maximum stretch on these curves. The values given in table 4 are the computed static energies for specimens having the average length of the impact-test specimens when loaded to failure of the first strand.

TABLE 4.—*Computed total static energy required to break one strand of specimens having the average length of those used for the impact tests*

Nominal length and fiber	Energy
	ft-lb
5-ft sisal	980
10-ft sisal	1,860
5-ft nylon	3,190
10-ft nylon	6,490

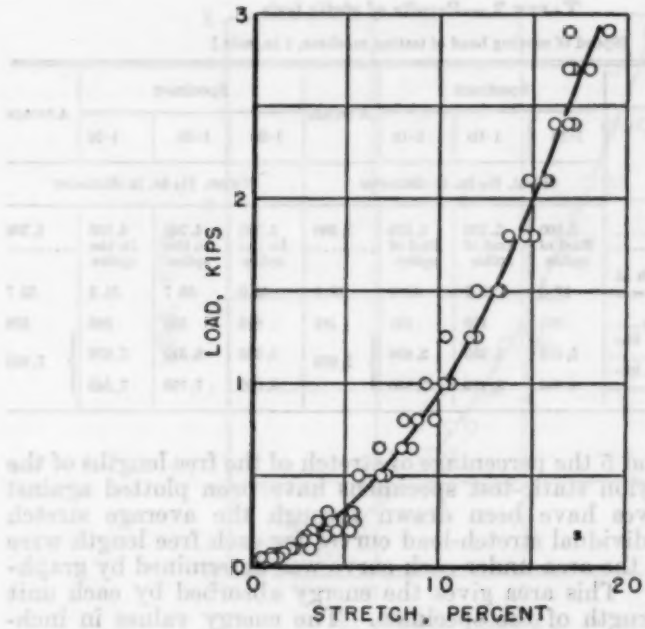

FIGURE 4.—*Load-stretch curve for free length of sisal static-test specimens.*

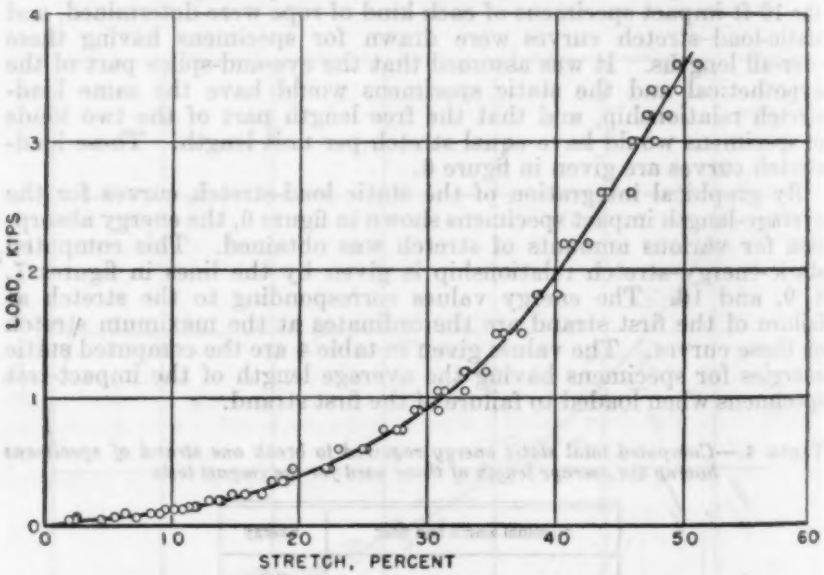

FIGURE 5.—*Load-stretch curve for free length of nylon static-test specimens.*

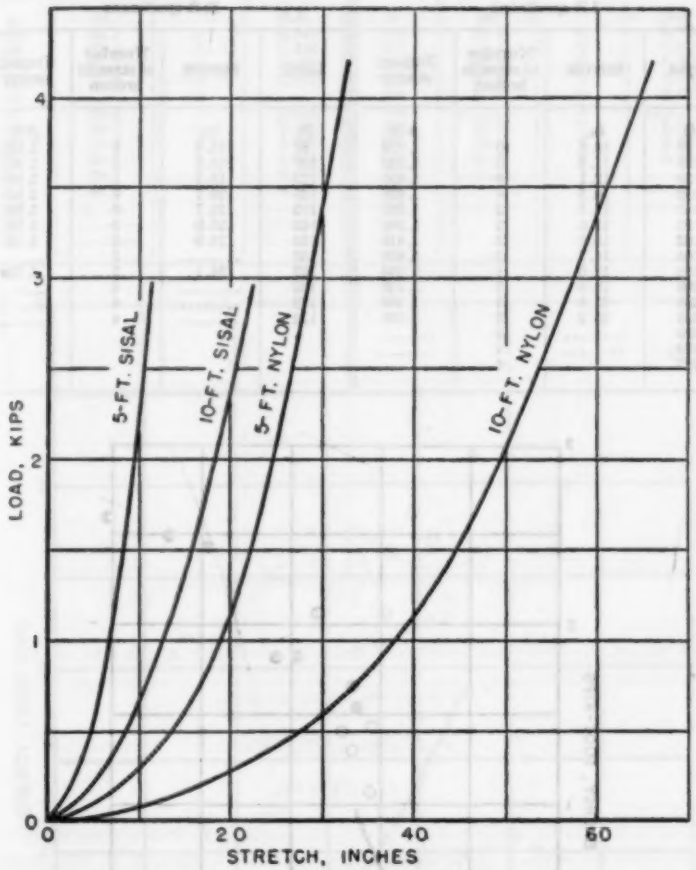

FIGURE 6.—*Load-stretch curves computed from static-test data for impact-test specimens.*

2. IMPACT TESTS

The results of the impact tests are given in tables 5 and 6 and in figures 7, 8, 9, and 10.

TABLE 5.—*Results of impact tests of four-strand 9/16-in.-diameter sisal rope*

[Height of drop of load, twice the length of the specimen. Each specimen impacted once only]

5-ft specimens				10-ft specimens			
Load	Stretch	Number of strands broken	Impact energy	Load	Stretch	Number of strands broken	Impact energy
lb	*in.*		*ft-lb*	*lb*	*in.*		*ft-lb*
99	10.6	0	1,070	97	16.6	0	2,080
119	11.6	0	1,300	107	18.1	0	2,300
129	12.1	0	1,400	122	18.4	1	2,640
132	10.5	0	1,430	123	20.7	0	2,690
142	11.3	2	1,530	132	19.7	0	2,860
152	11.6	2	1,660	142	23.0	3	3,150
162	15.9	3	1,810	142	24.9	3	3,150
164	14.7	2	1,830	152	.....	3	.....
184	13.6	1	2,060	162	34.1	3	3,700
208	19.6	3	2,430	162	.....	4	.....
208	21.8	3	2,400	172	.....	4	.....
214	25.2	3	2,500	172	.....	4	.....
219	.....	3	.....				
219	.....	4	.....				
233	.....	4	.....				

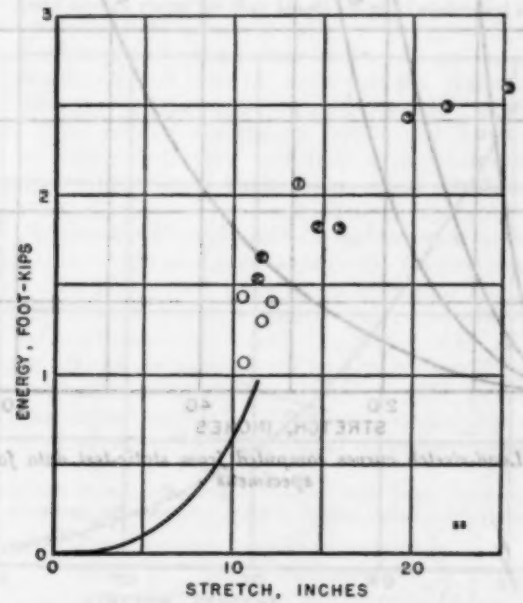

FIGURE 7.—*Energy-stretch relationships for 5-foot sisal specimens.*

The curve was computed from static data. The circles represent results of impact tests, and the numbers refer to number of broken strands.

TABLE 6.—*Results of impact tests of three-strand, 7/8-in. diameter, nylon rope*

[Height of drop of load, twice the length of the specimen. Each specimen impacted once only]

5-ft specimens				10-ft specimens			
Load	Stretch	Number of strands broken	Impact energy	Load	Stretch	Number of strands broken	Impact energy
lb	*in.*		*ft-lb*	*lb*	*in.*		*ft-lb*
264	28.1	0	3,230	268	55.0	0	6,740
268	27.5	0	3,340	278	55.4	0	7,010
274	29.2	0	3,510	288	56.2	0	7,250
278	27.9	0	3,500	298	58.5	0	7,590
278	.....	3	.....	298	57.4	0	7,620
288	28.2	0	3,620	298	.....	3	.....
294	29.7	0	3,770	308	58.2	0	7,840
298	28.5	0	3,730	328	62.0	0	8,550
308	28.7	0	3,870	328	61.6	0	8,570
309	29.1	0	3,940	328	.....	3	.....
319	29.0	2	4,370	338	.....	3	.....
319	.....	3	.....	338	.....	3	.....
319	.....	3	.....				
329	.....	3	.....				

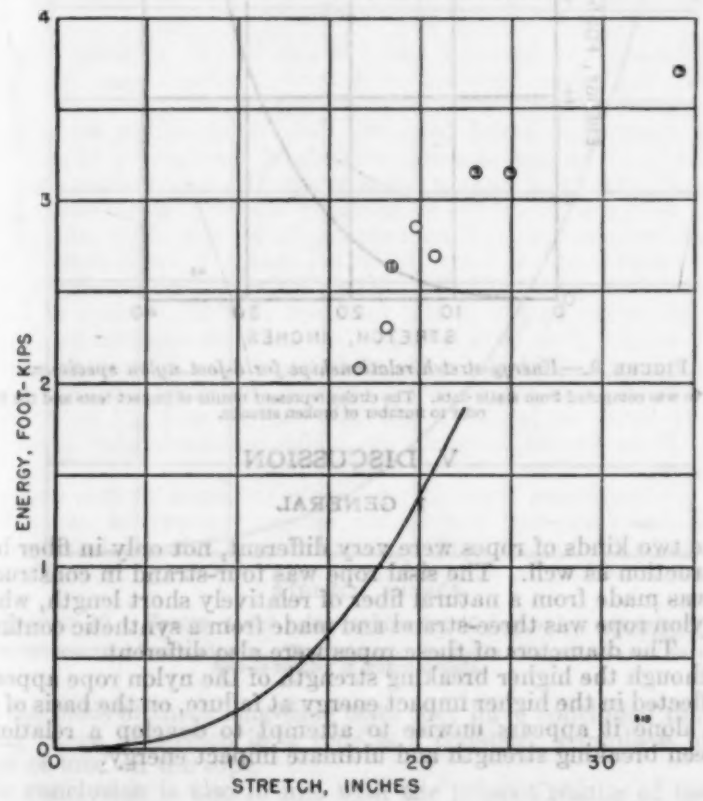

FIGURE 8.—*Energy-stretch relationships for 10-foot sisal specimens.*

The curve was computed from static data. The circles represent results of impact tests and the numbers refer to number of broken strands.

The impact energy absorbed by each specimen was computed by multiplying the weight by the total height of drop, which included the stretch of the specimen, and adding the stretch times the weight of the weight pan.

Stretch under impact load was plotted against the energy computed in each case and these are plotted as circles in figures 7, 8, 9, and 10. The numbers in the circles refer to the number of broken strands. Where no number appears in the circle, the specimen did not fail under the impact load.

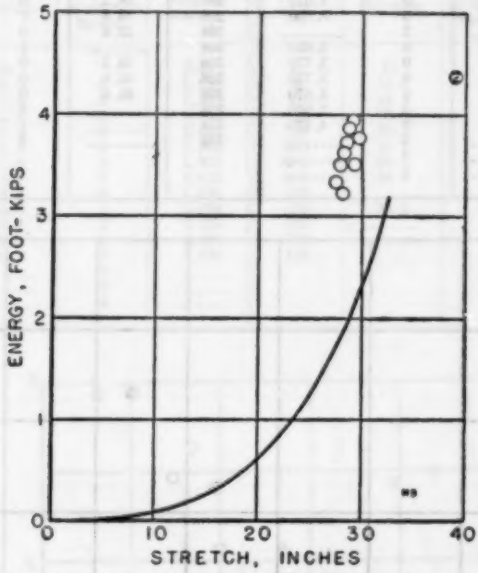

FIGURE 9.—*Energy-stretch relationships for 5-foot nylon specimens.*

The curve was computed from static data. The circles represent results of impact tests and the numbers refer to number of broken strands.

V. DISCUSSION

1. GENERAL

The two kinds of ropes were very different, not only in fiber but in construction as well. The sisal rope was four-strand in construction, and was made from a natural fiber of relatively short length, whereas the nylon rope was three-strand and made from a synthetic continuous fiber. The diameters of these ropes were also different.

Although the higher breaking strength of the nylon rope appears to be reflected in the higher impact energy at failure, on the basis of these tests alone it appears unwise to attempt to develop a relationship between breaking strength and ultimate impact energy.

2. STRETCH

Lutts and Himmelfarb [1] have found that when cotton and manila ropes are subjected to dead loads considerably below their normal breaking strengths they continue to stretch with time until limiting values are reached and the ropes fail. These limiting values were practically equal to the stretch at the breaking point as determined by static tests in a testing machine.

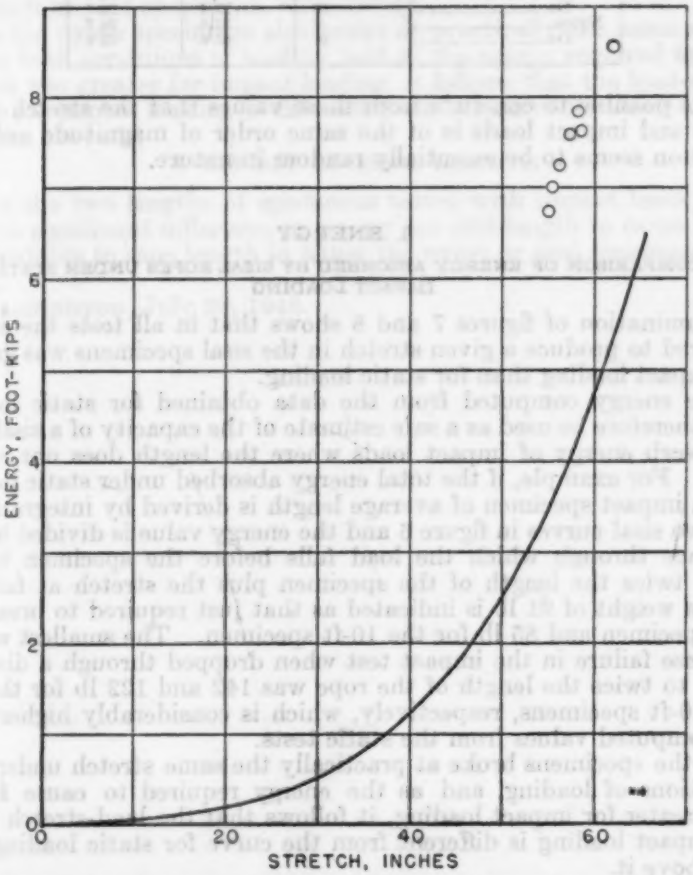

FIGURE 10.—*Energy-stretch relationships for 10-foot nylon specimens.*

The curve was computed from static data. The circles represent results of impact tests and the numbers refer to number of broken strands.

On the basis of these long-time tests they have concluded that the limiting range of stretch in a rope is a constant, regardless of the tension or load on the rope.

This conclusion is also in line with the present results of tests of sisal and of nylon ropes subjected to impact loads. Table 7 gives a comparison of the stretch of the static and the impact specimens.

[1] Carlton G. Lutts and David Himmelfarb, The Creep phenomenon in ropes and cords, Proc. Am. Soc. Testing Materials, pt. I, 40, 1251 (1940).

TABLE 7.—*Stretch of static and of impact specimens*

Fiber	Nominal length of specimens	Computed average stretch at maximum static load	Maximum stretch of a specimen which did not break under impact load
	ft	*in.*	*in.*
Sisal	5	11.4	12.1
Do	10	22.4	20.7
Nylon	5	32.6	29.7
Do	10	65.6	62.0

It is possible to conclude from these values that the stretch under static and impact loads is of the same order of magnitude and any variation seems to be essentially random in nature.

3. ENERGY

(a) COMPARISON OF ENERGY ABSORBED BY SISAL ROPES UNDER STATIC AND IMPACT LOADING

Examination of figures 7 and 8 shows that in all tests the energy required to produce a given stretch in the sisal specimens was greater for impact loading than for static loading.

The energy computed from the data obtained for static loading may therefore be used as a safe estimate of the capacity of a sisal rope to absorb energy of impact loads where the length does not exceed 10 ft. For example, if the total energy absorbed under static loading by an impact specimen of average length is derived by integration of the two sisal curves in figure 6 and the energy value is divided by the distance through which the load falls before the specimen breaks (i. e., twice the length of the specimen plus the stretch at failure), then a weight of 91 lb is indicated as that just required to break the 5-ft specimen and 85 lb for the 10-ft specimen. The smallest weight to cause failure in the impact test when dropped through a distance equal to twice the length of the rope was 142 and 122 lb for the 5-ft and 10-ft specimens, respectively, which is considerably higher than the computed values from the static tests.

As the specimens broke at practically the same stretch under both conditions of loading, and as the energy required to cause failure was greater for impact loading, it follows that the load-stretch curve for impact loading is different from the curve for static loading and lies above it.

(b) COMPARISON OF ENERGY ABSORBED BY NYLON ROPES UNDER STATIC AND IMPACT LOADING

Figures 9 and 10 show that the energy required to produce a given stretch in the nylon specimens was greater for impact loading then for static loading. Therefore, the energy computed from static-test load-stretch data may also be used to obtain a safe estimate of the impact-energy capacity of a nylon rope of the length used in these tests.

If the energy absorbed under static loading by an impact specimen of average length is derived by integration of the two nylon curves in figure 6, and this energy value is divided by the distance through which the load falls before the specimen breaks (i. e., twice the length of the specimen plus the stretch at failure), a weight of 247 lb is indicated as that just required to break the 5-ft specimen and 249 lb for the 10-ft specimen. Both of these values are below the weights determined experimentally, namely, 278 and 298 lb for the 5-ft and the 10-ft impact specimens, respectively.

As the nylon specimens also broke at practically the same stretch under both conditions of loading, and as the energy required to cause failure was greater for impact loading, it follows that the load-stretch curve for impact loading is different from the curve for static loading and lies above it.

4. EFFECT OF ROPE LENGTH

For the two lengths of specimens tested with impact loads, there was no significant difference in energy per unit length to cause failure attributable to rope length in either the nylon or sisal specimens.

WASHINGTON, July 20, 1945.

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OXIDATION OF GALACTURONIC ACID AND OF 5-KETO-GLUCONIC ACID IN ALKALINE SOLUTION

By Horace S. Isbell and Nancy B. Holt

ABSTRACT

In the present investigation determinations were made of the quantities of oxalate, tartrate, and trihydroxyglutarate formed by the oxidation of galacturonic acid and of 5-keto-gluconic acid in the presence of various bases and various concentrations of the base. Although preliminary measurements indicate that the proportions of the products can be altered by use of catalysts, this report is restricted to the results obtained without the addition of catalytic substances. Oxidation of sodium galacturonate with oxygen in 1-*N* sodium hydroxide solution gave oxalate, D-tartrate (levo), and D-*arabo*-trihydroxyglutarate in yields of 0.10, 0.10, and 0.45 mole, respectively, per mole of galacturonate. Oxidation of sodium 5-keto-gluconate under like conditions gave oxalate, L-tartrate (dextro), and *xylo*-trihydroxyglutarate in yields of 0.29, 0.10, and 0.45 mole, respectively, per mole of sodium 5-keto-gluconate. Directions are included for the preparation of potassium D-*arabo*-trihydroxyglutarate from galacturonic acid.

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I. INTRODUCTION

The development of relatively simple methods for the preparation of salts of galacturonic acid [1][1] and of 5-keto-gluconic acid [2] makes these substances readily available for the investigation of possible uses. The preparation of L-tartaric acid (dextrorotatory)[2] from 5-keto-gluconic acid and the preparation of D-*arabo*-trihydroxyglutaric acid from galacturonic acid are reported in the patent literature [3, 4]. The processes for the preparation of the two products are

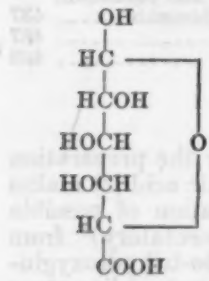
[1] Figures in brackets indicate the literature references at the end of this paper.

[2] Dextrorotatory tartaric acid is commonly called *d*-tartaric acid. The "*d*" refers to the direction of optical rotation, and should not be confused with the "D" used to indicate configuration in the carbohydrate field. Dextrorotatory tartaric acid is configurationally related to L-glyceraldehyde, the substance used for the D and L classification of the carbohydrates. In this paper it is designated L-tartaric acid.

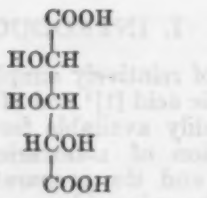
similar, but it would appear from the patent specifications that 5-keto-gluconic acid on oxidative cleavage yields largely a 4-carbon dibasic acid (tartaric), whereas galacturonic acid yields largely a 5-carbon dibasic acid (trihydroxyglutaric). Since both materials might be expected to yield both 4- and 5-carbon dibasic acids, further investigation of the oxidative cleavage of the two substances seemed desirable.

5-Keto-gluconic acid and galacturonic acid are sugars having a terminal carboxyl group in place of the terminal CH_2OH group characteristic of the simple sugars. Thus galacturonic acid is a substituted D-galactose and 5-keto-gluconic acid is a substituted L-sorbose. The investigations of Nef, Spoehr, Anderson, Evans, Glattfeld, and others [5] have shown that the oxidation of reducing sugars in alkaline solution gives rise to numerous products. In the galactose series, it has been shown that oxidative cleavage of the bond between carbons 1 and 2 yields D-lyxonic and formic acids; cleavage of the 2,-3-bond yields D-threonic and glycolic acids; and cleavage of the 3,-4-bond yields two molecules of glyceric acid. In addition to these acids, small quantities of carbon dioxide and oxalic acid are formed.

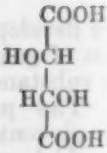
With galacturonic acid, I, oxidative cleavage of the 1,2-bond would be expected to yield formic acid and D-*arabo*-trihydroxyglutaric acid, II, and cleavage of the 2,3-bond, glycolic acid, and D-tartaric acid, III. With 5-keto-gluconic acid, IV, oxidative cleavage of the bond between carbons 5 and 6 or between carbons 4 and 5, would be expected to yield products quite similar to those formed from galacturonic acid. The 5-carbon dibasic acid in this case would be *xylo*-trihydroxyglutaric acid, V, and the 4-carbon dibasic acid, L-tartaric acid, VI. Oxidative cleavage of the 3,4-bond of either galacturonic acid or 5-keto-gluconic acid would be expected to yield D,L-glyceric acid and tartronic acid. The separation and quantitative determination of all the products formed by the oxidation of the two materials would constitute a long investigation, which does not seem warranted at this time. The present study has been restricted to the determination of the amounts of oxalic, tartaric, and trihydroxyglutaric acid formed in the reaction.



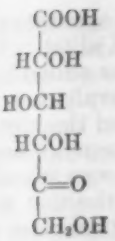
I. D-Galacturonic acid.



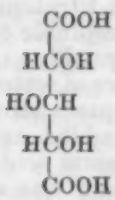
II. D-*arabo*-Trihydroxyglutaric acid.



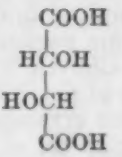
III. D-Tartaric acid.



IV. 5-Keto-D-gluconic acid.



V. *xylo*-Trihydroxy-glutaric acid.



VI. L-Tartaric acid.

II. EXPERIMENTAL METHODS

1. OXIDATION METHOD

The oxidation reactions were conducted in a Parr apparatus of the type used for low-pressure hydrogenation. The aqueous alkali required for each experiment was placed in the glass reaction flask and saturated with oxygen at room temperature. The material to be oxidized, usually 0.05 equivalent, was added quickly, connections were made with the oxygen supply, and the mixture was shaken vigorously with oxygen at a pressure of 20 pounds. Most of the oxidation occurred in the course of several hours, but in order to maintain uniform conditions and be certain that the reaction was complete, shaking was continued for a period of 48 hours. The reaction mixture was then analyzed or used for the preparation of the desired compounds. At the end of the reaction period a test for copper-reducing substances by means of Benedict's reagent was negative.

2. DETERMINATION OF OXALATE, TARTRATE, AND TRIHYDROXYGLUTARATE

In the experiments in which calcium hydroxide was used as a base a precipitate was formed which consisted largely of calcium oxalate and basic calcium salts of tartaric acid and trihydroxyglutaric acid. When a soluble hydroxide was used, an equivalent amount of calcium chloride was added to the solution containing the oxidation products to precipitate the insoluble calcium salts. The precipitate was collected on a filter, washed with lime water, dried, and weighed. A calcium determination was made on the dried material to facilitate subsequent work.

Oxalate was determined on a sample of the dried calcium salts by dissolving them in acid and precipitating calcium oxalate by the addition of ammonium hydroxide to neutrality. The simultaneous precipitation of calcium tartrate was prevented by the addition of 5 g of ammonium acetate per 100 ml of solution.[3] The calcium oxalate was precipitated and titrated with potassium permanganate in the usual manner.

[3] Boric acid may be used also to avoid interference of tartaric acid in the determination of oxalate. See "Analysis of Foods" by A. L. Winton and K. B. Winton, page 216 (John Wiley & Sons, Inc., New York N. Y., 1945).

The determination of tartrate was based upon the separation of potassium acid tartrate and its titration with standard alkali. Two grams of the dried mixture of insoluble calcium salts was added to an amount of finely powdered crystalline oxalic acid equivalent to the calcium present. Four milliliters of water was added, and the mixture was allowed to stand with frequent stirring. After about 24 hours, 1.8 g of potassium acetate was added, and the material was stirred to induce crystallization of potassium acid tartrate. At the end of an hour 18 ml of glacial acetic acid was added, and the mixture was allowed to stand for 24 hours. Fifteen milliliters of 95-percent alcohol was then added, and after an additional 24 hours the mixture was filtered on a Gooch crucible, washed with 5 ml of 95-percent aqueous acetic acid, 5 ml of glacial acetic acid, and finally with 95-percent alcohol. The filtrate and washings were set aside for the determination of trihydroxyglutaric acid. The crucible and contents were dried at 105° C in a vacuum oven until free from volatile acids. The dry material, largely calcium oxalate and potassium acid tartrate, was suspended in water, and the potassium acid tartrate was determined by titration with potassium hydroxide.

The determination of trihydroxyglutarate was based upon precipitation as the insoluble lead trihydroxyglutarate. The filtrate from the tartrate determination was evaporated to dryness at room temperature in a stream of air. The residue was dissolved in a few milliliters of water, and an aqueous solution of lead acetate was added in amount sufficient to convert the potassium trihydroxyglutarate to the insoluble lead salt. A large excess of lead acetate was avoided. After 18 hours, the lead salt was filtered on a weighed Gooch crucible, washed with water, dried at 60° C in a vacuum oven, and weighed.

In order to establish the identity of the lead salt derived from galacturonic acid, it was converted to the characteristic crystalline potassium salt. The optical rotation and analysis showed that the product was potassium D-*arabo*-trihydroxyglutarate.

To identify the lead salt from 5-keto-gluconic acid, it was decomposed with hydrogen sulfide, and the acid was converted to the bisphenylhydrazide. The melting point and analysis agreed with those of the previously known bisphenylhydrazide of *xylo*-trihydroxyglutaric acid.

3. PREPARATION OF POTASSIUM ACID D-TARTRATE (LEVO) AND POTASSIUM D-*ARABO*-TRIHYDROXYGLUTARATE FROM SODIUM GALACTURONATE

For the separation of potassium trihydroxyglutarate a method was employed which is somewhat similar to that used for the analysis of the oxidation mixture. The sodium galacturonate (0.15 mole) was dissolved in 600 ml of normal sodium hydroxide and oxidized in the manner described on page 435. When oxidation was complete, the reaction product was treated with 45 g of calcium chloride. After several hours, the resulting mixture of difficultly soluble calcium salts was separated by filtration, washed with lime water, and finally suspended in water. Sufficient oxalic acid was added to convert the salts to calcium oxalate and the free acids. It was necessary to digest the mixture on the steam bath for several hours to effect complete conversion of the salts. The calcium oxalate was separated by filtra-

tion and discarded. The filtrate was divided into two equal parts, one of which was neutralized with potassium hydroxide. The two portions were then combined, and the solution was concentrated to a volume of 100 ml. Methyl alcohol was added to the point of turbidity, and the solution was allowed to stand until crystallization of potassium acid tartrate was complete (2 days). The crystals were collected on a filter, washed with 50-percent aqueous alcohol, and dried. The crude potassium acid tartrate weighed 4.22 g. After one recrystallization from water, 2.8 g of pure potassium acid D-tartrate was obtained. This corresponds to 0.10 mole of tartrate per mole of sodium galacturonate.

The filtrate and mother liquor remaining after separation of the potassium acid tartrate were combined, and the resulting solution was neutralized with potassium hydroxide and evaporated nearly to dryness. The crystals that formed were separated by filtration, washed with 50-percent aqueous alcohol, and dried. The material thus obtained weighed 17.3 g, corresponding to a yield of 0.45 mole of potassium trihydroxyglutarate per mole of sodium galacturonate. The crude material had a specific rotation of $-8.4°$. After recrystallization of the compound from water, $[\alpha]_D^{20} = -8.6°$ (water, c=4). The specific rotation of potassium D-*arabo*-trihydroxyglutarate reported in the literature is $-8.7°$ [6]. *Analysis:* Calculated for $K_2C_5H_6O_7$: C, 23.43; H, 2.36; K, 30.51. Found: C, 23.4; H, 2.7; K, 30.5.

4. PREPARATION OF POTASSIUM ACID L-TARTRATE (DEXTRO) AND POTASSIUM *XYLO*-TRIHYDROXYGLUTARATE FROM CALCIUM 5-KETO-GLUCONATE

Sodium carbonate (5.3 g) was added to 24 g (0.1 equivalent) of calcium 5-keto-gluconate suspended in 200 ml of water. After removal of the resulting calcium carbonate by filtration, 200 ml of 2-*N* sodium hydroxide was added and the sodium 5-keto-gluconate was oxidized with oxygen. Potassium acid L-tartrate and potassium *xylo*-trihydroxyglutarate were prepared from the reaction mixture by the procedure described in the previous section for the preparation of potassium acid D-tartrate and potassium D-*arabo*-trihydroxyglutarate. The potassium acid L-tartrate weighed 0.95 g and was substantially pure. The potassium *xylo*-trihydroxyglutarate did not crystallize and was obtained only as an amorphous solid. By treatment with lead acetate it was converted to lead *xylo*-trihydroxyglutarate. The lead salt (17 g) was decomposed with hydrogen sulfide, and the resulting acid was converted to the characteristic bisphenylhydrazide. The latter substance melted at 210° C in accordance with the value reported by Fischer [7].

III. DISCUSSION OF RESULTS

The results obtained by application of the foregoing methods to a number of salts of galacturonic acid and of 5-keto-gluconic acid are given in table 1. It will be recalled that oxidation of 5-keto-gluconic acid is reported to yield dextrorotatory tartaric acid [3], whereas galacturonic acid is reported to yield D-*arabo*-trihydroxyglutarate [4]. In the experiments given here, trihydroxyglutaric acid was obtained from both materials in approximately 45-percent yield, and tartaric

acid in approximately 10-percent yield. Thus, on oxidation with oxygen in alkaline solution, in the absence of a catalyst, both 5-keto-gluconic acid and galacturonic acid yield the corresponding 5-carbon dibasic acids in substantial quantities. Four-carbon dibasic acids are formed from the same substances in smaller yields.

TABLE 1.—*Oxidation of galacturonic acid and 5-keto-gluconic acid in alkaline solution*

Substance oxidized (0.05 equivalent)	Alkaline medium	Products (moles per equivalent of substance oxidized)		
		Oxalate	Tartrate	Trihydroxyglutarate
Potassium galacturonate	200 ml of 1-*N* KOH	0.08	0.13	0.47
Sodium galacturonate	200 ml of 1-*N* NaOH	.10	.10	.45
Do	200 ml of 2-*N* NaOH	.10	.09	.48
Sodium calcium galacturonate	200 ml of 1-*N* NaOH	.17	.09	.41
Calcium galacturonate	200 ml of water + 15 g of CaO	.41	.11	.34
Do	200 ml of water + 15 g of CaO+10 g of calcium acetate.	.44	.10	.20
Sodium 5-keto-gluconate	200 ml of 1-*N* NaOH	.29	.10	.45
Calcium 5-keto-gluconate	200 ml of water +15 g of CaO	.31	.11	.20

In all the experiments oxalic acid was formed in addition to tartaric acid and trihydroxyglutaric acids. Power and Upson [8] have found that air oxidation of both glucose and fructose in the presence of calcium hydroxide yields calcium oxalate in relatively large quantities, whereas air oxidation in the presence of sodium hydroxide produces little or none. Our results with galacturonic acid and 5-keto-gluconic acid show that these substances also give higher yields of oxalate with calcium hydroxide than with either sodium or potassium hydroxide. The yields of tartaric acid and trihydroxyglutaric acid obtained with calcium hydroxide are less than those obtained with alkali metal hydroxides. The addition of calcium acetate to the calcium hydroxide mixture caused only a small change in the amounts of oxalate and tartrate, but there was a substantial decrease in the amount of trihydroxyglutarate formed.

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